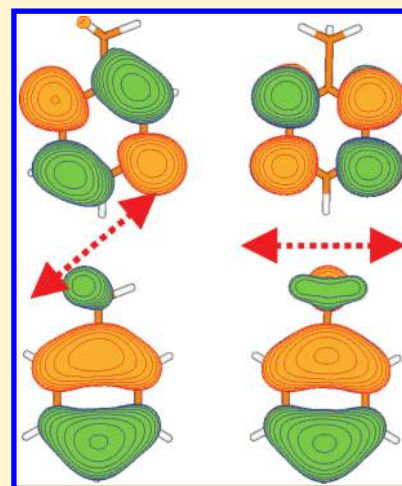


How and Why Do Transition Dipole Moment Orientations Depend on Conformer Structure?

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S Supporting Information

ABSTRACT: A remarkable influence of the orientation of a polar side chain on the direction of the $S_1 \leftarrow S_0$ transition dipole moment of monosubstituted benzenes was previously reported from high-resolution electronic spectroscopy. In search for a more general understanding of this non-Condon behavior, we investigated ethylamino-substituted indole and benzene (tryptamine and 2-phenylethylamine) using ab initio theory and compared the results to rotationally resolved laser-induced fluorescence measurements. The interaction of the ethylamino side chain with the benzene chromophore can evoke a rotation and a change of ordering of the molecular orbitals involved in the excitation, leading to state mixing and large changes in the orientation of the excited-state transition dipole moment. These changes are much less pronounced in tryptamine with the indole chromophore, where a rotation of the transition dipole moment is attributed to Rydberg contributions of the nitrogen atom of the chromophore. For phenylethylamine, a strong dependence of the oscillator strengths of the lowest two singlet states from the conformation of the side chain is found, which makes the use of experimental vibronic intensities for assessment of relative conformer stabilities at least questionable.



1. INTRODUCTION

The interaction between a flexible polar side chain and a chromophore to which it is connected covalently has found considerable interest over many years because it mimics the different stabilizations of electronic states by its direct molecular surrounding. Such interactions play an important role in the photophysics of aromatic chromophores, for example, in native peptides. In some cases, it is possible to monitor the influence of the side chain on the conformers by determination of the orientation of the $S_n \leftarrow S_0$ electronic transition dipole moment (TDM) for the different chromophores. In electronic spectroscopy, the perturbing light field of the irradiating photon(s) interacts with the wave functions of the electrons in the two electronic states involved in the transition. The TDM is the dipole moment of the oscillating charge density and a measure of electronic charge that is shifted during the excitation. For a $S_1 \leftarrow S_0$ transition, it is defined as

$$\langle \mu_{\text{TDM}} \rangle = \int \Psi_{S_1}^* \hat{\mu} \Psi_{S_0} d\tau_e \quad (1)$$

Ψ_{S_1} and Ψ_{S_0} are the wave functions of the corresponding states S_1 and S_0 , $\hat{\mu}$ is the electronic dipole operator, and the integral runs over the coordinates of all electrons. Changes in the orientation of the TDM with respect to the chromophore describe the modification of the electronic structure, induced

by its conformation in at least one electronic state involved. This change in electronic structure is accompanied by a change in reactivity. Knowledge of these mechanisms is indispensable when discussing the photophysics of molecular excited-state properties.

A lot of what we know about the interaction between a chromophore and an attached side chain was contributed to by the groups of Pratt and Simons.^{1–7} They ascertained the inertial and electronic contributions which are responsible for the rotation of the TDM. Analysis of partly or fully rotationally resolved electronic spectra yields the projection of the TDM onto the principal axis system (PAS) of a molecule. As the conformation changes, the PAS rotates, and consequently, the orientation of the TDM within this frame changes. This inertial contribution is easy to deal with as soon as the conformation of the molecule is known. Electronic contributions to the orientation of the TDM on the other hand are far more difficult to handle. Hepworth et al. analyzed the rotationally resolved fluorescence excitation spectra of 3-hydroxy benzoic acid esters and reported that, within the experimental error, a methyl ester

Special Issue: David W. Pratt Festschrift

Received: January 17, 2011

Revised: February 24, 2011

Published: April 18, 2011

group attached in the 3-position to phenol makes a constant electronic contribution to the orientation of the TDM in the molecular frame, independent of its orientation.¹ The influence of the hydroxyl group on the other hand depends much more on its orientation with respect to the ester group. In a following publication, the authors report of a small rotation of the TDM in different 3-aminobenzoic acid esters.³

The location of a polar side chain above the aromatic plane may have a remarkably large influence on the orientation of the TDM. The loss of symmetry in some conformers was postulated to be one of the main reasons, resulting in an increase of the number of single-electron excitations that contribute to the electronic excitation, such as in 3-phenyl-1-propionic acid.⁴ The importance of this interaction was demonstrated by Dickinson et al. in a study on *n*-propyl- and *n*-butylbenzene.⁵ Although these side chains lack polar groups, all gauche conformations show a rotation of the TDM. The effect of symmetry reduction alone seems not to turn the balance because no effect for asymmetric anti conformers could be detected. The bottom line of these works is that the loss of symmetry allows the possibility of state mixing, consistent with changes in the orientation of the $S_1 \leftarrow S_0$ TDM. The degree of mixing will depend on the interaction between the ring and the side chain. Dickinson et al. could substantiate this interaction by researching 2-phenylethylalcohol and 2-phenylethylamine.⁶ They report that the degree of rotation of the TDM in the gauche conformer is modulated by the hydrogen-bonding interaction between the terminal hydroxyl or amino hydrogen atom of the side chain and the π -system of the ring. The most thorough theoretical approach to this matter is ab initio work by Kroemer et al.² Five singly substituted benzene derivatives were studied in order to elucidate the interactions which are responsible for the observed rotations of the TDM.

The question arises whether these results also apply for less symmetric chromophores than benzene. Evidence is given by a publication of Hockridge et al.,⁷ who investigated 4-hydroxyphenylethanol; substitution of a OH group in the 4-position greatly reduces the sensitivity of the $\pi^* \leftarrow \pi$ transition to conformational changes. The system that we chose to further cast light on this subject is tryptamine (TRP). The conformational space of tryptamine has been the topic of several publications. Park et al. found six conformers in low-resolution laser-induced fluorescence (LIF) spectra and named them according to the relative intensity A–F.⁸ Rotationally resolved laser-induced fluorescence spectra were independently presented by Nguyen et al.⁹ and Schmitt et al.¹⁰ and resulted in the unequivocal assignment of the spectra to the seven conformers.

In the current study, we present a theoretical analysis of the TDM moment orientations in 2-phenylethylamine (PEA) and in 3-ethylaminoindole (tryptamine = TRP) and make comparison to the results of rotationally resolved electronic spectroscopy in order to unravel the very different interactions of the side chain with the chromophore.

2. THEORETICAL METHODS AND COMPUTATIONAL DETAILS

2.1. Geometry Optimization.

Structure optimizations were performed by employing the correlation-consistent polarized valence triple zeta (cc-pVTZ) basis from the Turbomole library.^{11,12} The equilibrium geometries of the electronic ground and excited states were determined using the approximate coupled-cluster singles and doubles model (CC2) in the approximation of the resolution of identity (RI). All optimizations and

Table 1. CC2/cc-pVTZ Calculated Relative Stabilities ΔE [kJ/mol] and Ground-State Rotational Constants A , B , and C [MHz] of the Five Most Stable 2-Phenylethylamine Conformers and of the of the Nine Most Stable Tryptamine Conformers^a

| PEA | ΔE | Calc. | | | Exp. ¹⁸ | | |
|-------------|------------|-------|------|-----|--------------------|---------|--------|
| | | A | B | C | A | B | C |
| Anti(out) | 0.000 | 4384 | 864 | 773 | 4396.16 | 857.41 | 766.80 |
| Gauche(out) | 1.041 | 3305 | 1107 | 972 | 3313.74 | 1079.28 | 959.20 |
| Anti(up) | 1.986 | 4341 | 862 | 772 | 4360.68 | 855.75 | 765.33 |
| Gauche(up) | 3.206 | 3270 | 1093 | 971 | 3287.71 | 1066.35 | 957.63 |
| Gauche(in) | 6.508 | 3412 | 1077 | 916 | | | |
| TRP | ΔE | Calc. | | | Exp. ⁹ | | |
| | | A | B | C | A | B | C |
| Gpy(out) | 0.000 | 1733 | 692 | 559 | 1731.02 | 682.04 | 551.56 |
| Anti(ph) | 1.051 | 1758 | 624 | 481 | 1767.97 | 618.39 | 478.27 |
| Anti(py) | 1.738 | 1764 | 621 | 479 | 1776.28 | 616.01 | 478.21 |
| Gph(up) | 2.156 | 1597 | 755 | 569 | 1605.11 | 737.84 | 561.51 |
| Anti(up) | 2.902 | 1755 | 621 | 479 | 1761.40 | 614.75 | 475.58 |
| Gpy(up) | 2.994 | 1712 | 691 | 558 | 1710.25 | 682.22 | 551.10 |
| Gph(out) | 4.279 | 1589 | 772 | 567 | 1590.07 | 754.94 | 561.18 |
| Gpy(in) | 5.238 | 2339 | 576 | 471 | | | |
| Gph(in) | 9.484 | 1565 | 759 | 544 | | | |

^a All calculations include ZPE corrections at the level of the optimization.

normal-mode analyses were carried out utilizing the Turbomole package, version 5.6.¹³

For the computation of singlet-state energies and wave functions, we used the combined density functional theory/multireference configuration interaction (DFT/MRCI) method by Grimme and Waletzke.¹⁴ This method was shown to yield excellent electronic spectra of organic molecules at reasonable computational expense. The configuration state functions (CSFs) in the MRCI expansion are built up from Kohn–Sham (KS) orbitals, optimized for the dominant closed-shell determinant of the electronic ground state employing the BH-LYP^{15,16} functional. All 62 valence electrons were correlated in the MRCI runs, and the eigenvalues and eigenvectors of eight singlet states were determined. The initial set of reference CSFs was generated automatically in a complete active space type procedure (including all single excitations from the five highest occupied molecular orbitals in the KS determinant to the five lowest virtual orbitals) and was then iteratively improved. The MRCI expansion was kept moderate by extensive configuration selection. The MRCI space was spanned by about 100 000 energy-selected single and double excitations (200 000 singlet CSFs) from approximately 45 reference configurations for PEA and 50 reference configurations for TRP.

3. RESULTS AND DISCUSSION

3.1. Electronic Ground-State Energies and Structures.

The electronic ground-state energies of the five most stable conformers of PEA and of the nine most stable conformers of TRP are calculated using DFT/MRCI on the CC2/cc-pVTZ optimized structures (cf. Table 1). The structures of the conformers investigated in this study are shown in Figures 2–4. The conformational space of PEA was investigated by Dickinson et al. using LIF and one- and two-color, mass-selected resonant two-photon

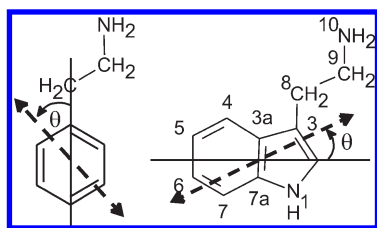


Figure 1. Atomic numbering for tryptamine and the definition of the polar angle θ (positive sign) for PEA and TRP. The axes, which define the angle θ in PEA and TRP, are the a -axes of the Anti(up) conformer and of indole, respectively.

ionization (R2PI) spectroscopy.⁶ They numbered the theoretically predicted conformers from I to V and could assign conformers II–V to observed spectroscopic features. The five conformers are the Gauche(in), the Gauche(up), the Gauche(out), the Anti(out), and the Anti(up) conformers, respectively. In this nomenclature, Gauche refers to the gauche orientation of the amino group, and “in”, “up”, and “out” describe the orientation of the amino lone pair.

The nomenclature for the different TRP conformers was introduced by Carney et al.¹⁷ Gpy (Gph) designates conformations in which the amino group is in gauche conformation and points to the pyrrole (phenyl) side of the indole chromophore. In all anti conformers, the amino group points away from the chromophore. The orientation of the amino group lone pair is described by the identifiers up, out, and in, like in PEA. Although the two in conformers of TRP, with the lone pair pointing to the indole ring, have similar ground-state energies as the other seven ones, they have never been observed experimentally. For the sake of completeness, the Gpy(in) and Gpy(in) conformers of tryptamine and the Gauche(in) conformer of PEA were included in this study. Interestingly, the structure evaluated for the Gpy(in) conformer of TRP deviates strongly from all other tryptamine conformers. The C₃–C₈ bond is rotated by 60° toward the pyrrole ring so that the terminal nitrogen atom of the side chain is located in the plane of the chromophore and a hydrogen bond is formed between the lone pair and H_{2a} (see Figures 1 and 4).

3.2. Transition Dipole Moments. The analysis of rovibronic line intensities in rotationally resolved electronic spectra yields the projection of the transition dipole moment vector onto the principal axes. In flexible molecules with several stable minima on the potential energy surface however, the position and orientation of the PAS depends on the actual conformation. In order to compare the orientations of the TDM vector of different conformers independently of the conformation, a reference frame has to be chosen into which all of the other coordinate systems have to be rotated. The most obvious choice is the PAS of the chromophore itself without the side chain.

To evaluate the experimentally determined transition dipole moments within this coordinate system, they have to be converted into Cartesian coordinates by using eq 2. Here, μ_α ($\alpha = a, b, c$) are the components of the transition dipole moment vector with respect to the principal axes a, b , and c , μ is the magnitude of the transition dipole moment, and ϕ and θ are the polar angles of the TDM in the PAS. As no information about the sign of the components can be extracted from the spectra, there are four different orientations which have to be taken into account (2^3 possible permutations of the sign divided by 2 as, for instance, the combination of only positive and only negative components yields the same vector). However, not all of these possibilities are

Table 2. Leading Contributions of Single-Electron Excitations to the Electronic Transition and Oscillator Strengths for All Conformers of PEA^a

| conformer | state | c | excitation | osc. strength | θ | $\theta^{\text{exp } 6}$ | state |
|-------------|-------|----------|------------|-----------------------|----------|--------------------------|-------|
| Anti(up) | S_1 | 0.67703 | 24 → 25 | 1.94×10^{-3} | +90 | +90 | L_b |
| | | 0.61209 | 23 → 26 | | | | |
| | S_2 | -0.79177 | 24 → 26 | 6.47×10^{-2} | ±0 | | L_a |
| | | 0.54405 | 23 → 25 | | | | |
| Anti(out) | S_1 | 0.69962 | 24 → 25 | 6.40×10^{-4} | +84 | +90 | L_b |
| | | -0.62435 | 23 → 26 | | | | |
| | S_2 | 0.75342 | 24 → 26 | 2.07×10^{-2} | -4 | | L_a |
| | | 0.61352 | 23 → 25 | | | | |
| Gauche(in) | S_1 | -0.64748 | 24 → 26 | 1.15×10^{-4} | -25 | - | L_b |
| | | 0.59123 | 23 → 25 | | | | |
| | S_2 | 0.71811 | 24 → 25 | 2.76×10^{-2} | -4 | | L_a |
| | | 0.55977 | 23 → 26 | | | | |
| Gauche(up) | S_1 | 0.56142 | 24 → 25 | 9.15×10^{-4} | +73 | +84(-56) | L_b |
| | | -0.46683 | 23 → 26 | | | | |
| | S_2 | 0.62670 | 24 → 26 | 2.94×10^{-2} | -20 | | L_a |
| | | 0.46354 | 23 → 25 | | | | |
| Gauche(out) | S_1 | -0.6147 | 24 → 25 | 5.56×10^{-4} | -80 | -88(+46) | L_b |
| | | -0.55333 | 23 → 26 | | | | |
| | S_2 | 0.66821 | 24 → 26 | 2.73×10^{-2} | -5 | | L_a |
| | | -0.54093 | 23 → 25 | | | | |

^aThe contributions of a single-electron excitation equals the square of the coefficient c . The HOMO is orbital 24, and the LUMO is 25. For a graphical overview over the frontier orbitals, refer to Figure 3.

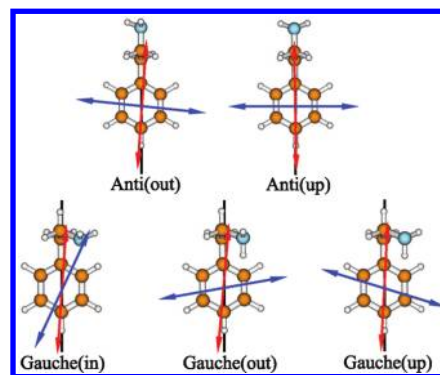


Figure 2. DFT/MRCI (cc-pVTZ) calculated transition dipole moments of 2-phenylethylamine. The L_a TDM is shown in red, and the L_b TDM is in blue. For comparison, the a -axis of the Anti(out) conformer is also displayed.

physically meaningful. Because all excitations of PEA and TRP take place in the (planar) chromophore, all TDM vectors exhibiting an angle ϕ , which deviates much from 90° in the PAS of the chromophore, can be neglected. From the remaining solutions, those were chosen which had the smallest deviation to the theoretical predictions.

$$\begin{aligned}
 \mu_a &= \mu \cdot \sin\phi \cdot \cos\theta \\
 \mu_b &= \mu \cdot \sin\phi \cdot \sin\theta \\
 \mu_c &= \mu \cdot \cos\phi
 \end{aligned}
 \quad (2)$$

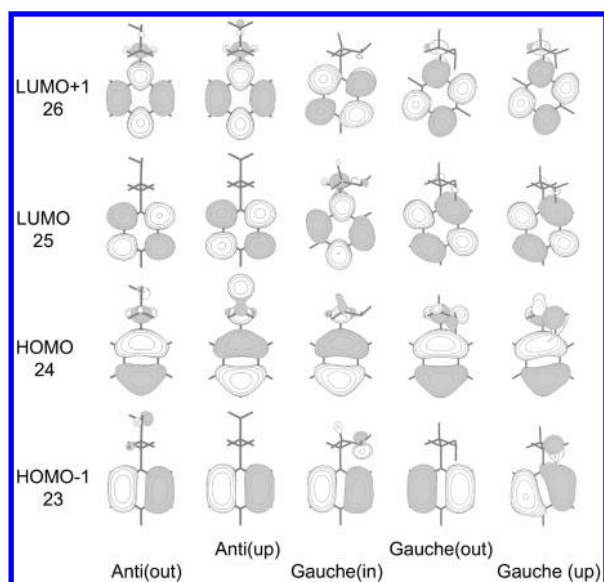


Figure 3. Frontier orbitals of the five 2-phenylethylamine conformers. Note the strong hyperconjugative effects in the HOMOs of the different conformers. LUMO and LUMO+1 are interchanged for Gauche(in) compared to the other conformers, as can be seen from the nodal structure. For the other Gauche conformers, LUMO and LUMO+1 are rotated with respect to the Anti conformers.

For all 2-phenylethylamine conformers, the reference frame is the C_s symmetric Anti(up) conformer. Here, the transition dipole moments of the L_a and L_b states are orthogonal to each other, the one of the L_b oriented parallel to the short-axis (b) of the chromophore.¹⁹

3.2.1. Transition Dipole Moments of PEA. The results for the orientations and magnitudes of the transition dipole moments from the DFT/MRCI calculations of the five PEA conformers are compiled in Table 2. The structures of all conformers are depicted in Figure 2 along with the theoretically predicted orientations of the TDM for both states concerned. The L_a TDM is drawn in red and the L_b TDM in blue. The angle θ in Table 2 is defined as follows; the side chain is located above the chromophore and rotated to the right. Turning the vector counterclockwise from the a -axis of the C_s symmetric Anti(up) conformer is defined as the positive direction.

From the comparison of the orientations and magnitudes of the TDMs, several facts are eye-catching: the transition dipole moments of the two lowest electronically excited states are nearly perpendicular to each other in all experimentally ascertained states. In the case of the Anti(up) conformer, the relative orientation ($\zeta = \theta(L_b) - \theta(L_a)$) is determined by symmetry to be exactly 90° , but even without a symmetry constraint, the minimum value of ζ for the other conformers is 74° for the Gauche(out) conformer. The only conformer, which deviates strongly is Gauche(in), which has a remarkably small angle ζ of 25° .

Interestingly, the orientation of the L_a TDM is only very slightly affected by the conformation of the side chain. The largest deviation in the θ angle (about 20°) is observed for the Gauche(up) conformer. Comparison to the values published by the Simons group⁶ shows that there is reasonable agreement in the theoretical predictions and experimental values. The experimental values for θ in Table 2 have been calculated from the experimentally determined projections of the transition dipole

moments, given in ref 6, according to our definition of the angle θ . Two different values result because only the projection to the inertial axis is determined from the experiment, and the sign of θ remains undetermined. Adding the angle for rotation of the inertial axis system of the respective conformer into the frame of the Anti(up) conformer results in the two different angles, given in Table 2.

A closer look at the molecular orbitals and their contributions to the transitions gives some insight into the factors resulting in dipole moment rotation due to conformational changes. In Figure 3, the main contributing frontier orbitals (HOMO–1 to LUMO+1) are depicted, and all excitations including their relative single-electron contributions are compiled in Table 2.

We start the analysis with the Anti(up) conformer because in this conformer, side chain–chromophore interactions are assumed to play the smallest role within the PEA conformers. The transition to the S_1 state consists of nearly equal contributions of LUMO \leftarrow HOMO and (LUMO+1) \leftarrow (HOMO–1). The TDM makes an angle of 90° with the inertial a -axis (it runs through the bonds, and historically, it is called the L_b). The oscillator strength of the S_1 state is smaller by 2 orders of magnitude compared to the S_2 (another signature of the L_b state; see Table 2). The S_2 state (L_a) is governed by LUMO \leftarrow (HOMO–1) and (LUMO+1) \leftarrow HOMO. The same behavior can be observed for the Anti(out) conformer with nearly identical coefficients. The Gauche(up) and Gauche(out) conformers show a considerable amount of state mixing of around 30% (Gauche(up)) and 20% (Gauche(out)) in both states. The molecular orbitals of these two conformers show a rotation of the nodal structure, especially for the unoccupied orbitals; the occupied orbitals are much less affected. An exception is Gauche(up), whose HOMO–1 is rotated significantly toward the side chain due to interactions with the amino group. Interestingly, the oscillator strengths for transition to the electronically excited states for the different conformers differ by an order of magnitude. Thus, the use of intensity information in jet spectra for assessing relative stabilities of conformers seems questionable. This is independent from the problem of vibrational and conformational cooling in the molecular beam, which might be incomplete.

The small angle between the TDMs of the Gauche(in) conformer points to a strong change in the electronic excitation compared to the other conformers. Inspection of the frontier orbitals in Figure 3 shows that the LUMO+1 orbital looks very similar to the LUMO of the Anti conformers, exhibiting a nodal plane along the short axis of the molecule in contrast to all other LUMO+1 orbitals. Both unoccupied orbitals are shifted to higher energies compared to the other conformers. Thus, the large rotation of the L_b TDM for Gauche(in) is a result of the altered ordering of molecular orbitals, which in turn is a consequence of the interactions between the lone pair and the aromatic ring, leading to an effective change in the excitation scheme. Moreover, we conclude that the changes of the orientation of the other gauche conformers are a result of the rotated electronic symmetry in the unoccupied orbitals, which are due to interactions of the electrons located at the ring and the lone pair of the amino group. The relative orientations of the TDM cannot be used as an argument for the probability of state mixing at least in PEA.

3.2.2. Transition Dipole Moments of TRP. The orientations of the electronic transition dipole moment of the nine TRP conformers, derived from DFT/MRCI calculations, are compiled in Table 3 and Figure 4.

The effect of the side chain positions on the orientations of the transition dipole moment vectors in TRP is much smaller than that for PEA. The theoretically predicted values for θ of the L_b

Table 3. Leading Contributions of Single-Electron Excitations to the Electronic Transition for All Conformers of Tryptamine Based on DFT/MRCI^a

| conformer | state | c | exc. | osc. | | θ | $\theta^{\text{exp } 9}$ | state |
|-----------|----------------|----------|---------|-------------------------|-----|----------|--------------------------|-------|
| | | | | strength | | | | |
| Anti(ph) | S ₁ | 0.74289 | 30 → 32 | 1.58 × 10 ⁻² | +49 | +37(+61) | L _b | |
| | | 0.49637 | 31 → 33 | | | | | |
| | S ₂ | -0.90959 | 31 → 32 | 1.02 × 10 ⁻¹ | -45 | | L _a | |
| Anti(py) | S ₁ | -0.74189 | 30 → 32 | 1.73 × 10 ⁻² | +47 | +37(+61) | L _b | |
| | | 0.50464 | 31 → 33 | | | | | |
| | S ₂ | 0.91128 | 31 → 32 | 1.05 × 10 ⁻¹ | -45 | | L _a | |
| Anti(up) | S ₁ | -0.73484 | 30 → 32 | 1.33 × 10 ⁻² | +50 | +65(+33) | L _b | |
| | | 0.44447 | 31 → 33 | | | | | |
| | S ₂ | -0.90766 | 31 → 32 | 9.76 × 10 ⁻² | -46 | | L _a | |
| Gph(out) | S ₁ | -0.73856 | 30 → 32 | 1.60 × 10 ⁻² | +56 | +64(+30) | L _b | |
| | | 0.41696 | 31 → 33 | | | | | |
| | S ₂ | 0.90530 | 31 → 32 | 1.05 × 10 ⁻¹ | -44 | | L _a | |
| Gph(up) | S ₁ | 0.74101 | 30 → 32 | 1.81 × 10 ⁻² | +44 | +34(+54) | L _b | |
| | | -0.54864 | 31 → 33 | | | | | |
| | S ₂ | -0.91353 | 31 → 32 | 1.11 × 10 ⁻¹ | -45 | | L _a | |
| Gph(in) | S ₁ | 0.73834 | 30 → 32 | 1.87 × 10 ⁻² | +58 | - | L _b | |
| | | -0.51843 | 31 → 35 | | | | | |
| | S ₂ | 0.89979 | 31 → 32 | 1.09 × 10 ⁻¹ | -44 | | L _a | |
| Gpy(out) | S ₁ | 0.74667 | 30 → 32 | 2.00 × 10 ⁻² | +48 | +49(+25) | L _b | |
| | | 0.53814 | 31 → 33 | | | | | |
| | S ₂ | 0.91213 | 31 → 32 | 1.03 × 10 ⁻¹ | -44 | | L _a | |
| Gpy(up) | S ₁ | 0.74456 | 30 → 32 | 1.97 × 10 ⁻² | +51 | +59(+37) | L _b | |
| | | -0.43838 | 31 → 33 | | | | | |
| | S ₂ | 0.90587 | 31 → 32 | 1.00 × 10 ⁻¹ | -45 | | L _a | |
| Gpy(in) | S ₁ | -0.73992 | 30 → 32 | 1.67 × 10 ⁻² | +41 | - | L _b | |
| | | 0.54851 | 31 → 34 | | | | | |
| | S ₂ | -0.91089 | 31 → 32 | 1.07 × 10 ⁻¹ | -41 | | L _a | |

^aThe contributions of a single-electron excitation equals the square of the coefficient *c*. The HOMO is orbital 31, and the LUMO is 32. For a graphical overview over the frontier orbitals refer to Figure 5.

state lie between 41 and 58°. Thus, the maximum change of the TDM orientation in TRP is about 17°, in contrast to 82° for PEA. The experimentally determined angles lie between 34 and 64°; therefore, they tend to vary more than predicted. The theoretically predicted values for θ of the L_a state are nearly constant at around -44°. The excitation scheme for TRP is compiled in Table 3. It illustrates that the major contribution to the S₁ excitation is LUMO ← (HOMO-1) with around 55% for all conformers, while the S₂ is always dominated by a LUMO ← HOMO transition. Like in PEA, the L_b state is lowest in energy for all conformers. Additional significant contributions to the excitation are seldom and always occur for the L_b, but quite in contrast to PEA, where these additional contributions effectively mix L_a and L_b, this is not the case for TRP; L_a and L_b never have a single-electron excitation in common that piles up to 5%.

For PEA, the occupied orbitals were nearly unaffected by the conformation, and this observation extends to the unoccupied orbitals in the case of TRP. Neglecting minor changes of electron density located at the side chain, the HOMO-1, HOMO, and LUMO are virtually the same for all conformers. This is the reason for the constant orientation of the TDM for L_a. The LUMO+1 of some conformers show influences of higher Rydberg orbitals, which are shifted down in energy. The higher

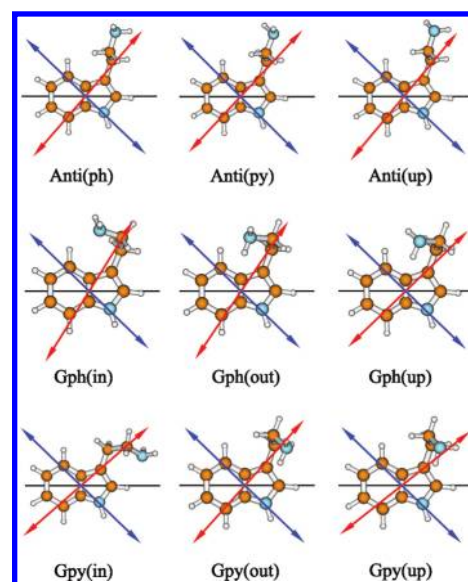


Figure 4. DFT/MRCI calculated transition dipole moments of tryptamine together with the *a*-axis of the chromophore indole. The L_a TDM is shown in red, and the L_b TDM is in blue.

orbitals differ in ordering and Rydberg contributions for the different conformers. A rotation of the nodal structure as observed for PEA is not taking place. Comparison of the orbitals involved in the excitation to the L_b and their depicted molecular orbitals reveals that the symmetry of the π -orbitals located in the chromophore determines which orbitals are involved. The LUMO+1 orbitals of all conformers except Gph(in) and Gpy(in) exhibit identical electron distribution of π -symmetry in the chromophore and differ only by the Rydberg contributions of the heteroatoms. The orbitals of the two exceptions are shifted higher in energy and become the LUMO+3 and LUMO+2, respectively. Therefore, the excitation scheme remains unchanged, as far as only the symmetry of the molecular orbitals in the chromophore is regarded. In a recent publication of our group on 5-methoxyindole, we reported exactly the same behavior; unoccupied π orbitals change energetic positions with Rydberg orbitals, but the (symmetry-adapted) single-electron excitation scheme stays the same as that in indole.²⁰

As the theoretical and experimental values vary much less than in PEA, deductions can only be made if both values are shifted significantly from the mean value in the same direction. For Gpy(up) and Gph(out), both values for θ tend to be significantly larger than the mean value. Interestingly, these two conformers are the only ones exhibiting a large Rydberg contribution at the nitrogen atom located in the five-membered ring in an orbital that is involved in the excitation.

3.2.3. Permanent Dipole Moments of PEA and TRP. The calculated permanent dipole moments of the three lowest singlet states of PEA and TRP are given in Table 4 along with experimental data from Lopez et al.¹⁸ for PEA and of Nguyen et al.²¹ for TRP.

Good agreement of our data with the experimental values is observed, which ensures us that DFT/MRCI is very capable of describing both permanent and transition dipole moments.

The theoretical predictions show that for TRP, excitation to the S₁ has no strong influence on the magnitude of the permanent electric dipole moment, quite in contrast to excitation to the S₂ state. Here, the permanent electric dipole moment is larger by

Table 4. Permanent Dipole Moments (in Debye) of the Two Lowest Excited Singlet States and the Polar Angles, Defined by Eq 2^a

| | S ₀ | | | S ₁ | | | S ₂ | | | S ₁ –S ₀ | | | S ₂ –S ₀ | | | exp. ^b | |
|-------------|----------------|-----|------|----------------|-----|------|----------------|-----|------|--------------------------------|----|-------|--------------------------------|-------|-------|-------------------|------------------|
| | θ | φ | μ | θ | φ | μ | θ | φ | μ | Δθ | Δφ | Δ μ | Δθ | Δφ | Δ μ | μ _{S0} | μ _{S1} |
| PEA | | | | | | | | | | | | | | | | | |
| Anti(up) | 0 | 0 | 1.20 | 0 | 0 | 1.17 | 0 | +38 | 1.18 | 0 | 0 | –0.03 | 0 | 38 | –0.02 | 1.36 | – |
| Anti(out) | +90 | +51 | 1.28 | +90 | +50 | 1.30 | +70 | +50 | 1.37 | 0 | –1 | +0.02 | –20 | –1 | +0.09 | 1.26 | – |
| Gauche(in) | +2 | +72 | 1.83 | +2 | +70 | 1.77 | –2 | +72 | 2.17 | 0 | –2 | –0.06 | 4 | 0 | +0.34 | – | – |
| Gauche(up) | –130 | +18 | 1.24 | –129 | +18 | 1.22 | –76 | +16 | 1.00 | –1 | 0 | –0.02 | 54 | –2 | –0.24 | 1.36 | – |
| Gauche(out) | –84 | +54 | 1.19 | –83 | +54 | 1.20 | +80 | +50 | 1.20 | –1 | 0 | +0.01 | –4 | +0.01 | 1.26 | – | – |
| TRP | | | | | | | | | | | | | | | | | |
| Anti(ph) | –40 | +71 | 2.97 | –28 | +72 | 3.05 | –15 | +81 | 6.34 | +12 | 1 | +0.08 | +25 | 10 | +3.37 | – | – |
| Anti(py) | –76 | +72 | 1.41 | –48 | +69 | 1.24 | –14 | +84 | 4.44 | +28 | –3 | –0.17 | +57 | 102 | +3.03 | – | – |
| Anti(up) | –48 | +63 | 2.74 | –32 | +64 | 2.76 | –15 | +79 | 5.88 | +16 | 1 | +0.02 | +33 | 16 | +3.14 | 2.6 | 2.5 |
| Gph(in) | +2 | +78 | 2.32 | +12 | +79 | 2.66 | +3 | +84 | 5.87 | +10 | 1 | +0.34 | +1 | 6 | +3.55 | – | – |
| Gph(out) | –42 | +75 | 2.95 | –30 | +75 | 2.96 | –16 | +82 | 6.12 | +12 | 0 | +0.01 | +26 | 7 | +3.17 | – | – |
| Gph(up) | –59 | +59 | 2.62 | –43 | +58 | 2.53 | –17 | +78 | 5.40 | +16 | –1 | –0.09 | +42 | 19 | +2.78 | 2.4 | 2.2 |
| Gpy(in) | +3 | +89 | 2.34 | +11 | +89 | 2.84 | +4 | +89 | 6.68 | +8 | 0 | +0.50 | +1 | 0 | +4.34 | – | – |
| Gpy(out) | –78 | +77 | 1.52 | –55 | +72 | 1.26 | –16 | +84 | 4.43 | +23 | –5 | –0.26 | +62 | 7 | +2.91 | 1.6 | 1.4 |
| Gpy(up) | –52 | +64 | 2.87 | –39 | +63 | 2.80 | –19 | +79 | 5.86 | +13 | –1 | –0.07 | +33 | 15 | +2.99 | 2.7 | 2.5 |

^a Additionally, changes of the angles and magnitudes induced by electronic excitation are given. ^b The experimental dipole moments for PEA have been taken from ref 18, and those of TRP are from ref 21.

a factor of 2–3, as to be expected for the L_a state in indole derivatives. Nguyen et al. observed in their study on TRP that, although the magnitude of the permanent electric dipole moment is not changed much by the excitation to the S₁, the orientation indeed is changed.²¹ As the changes happen to be mainly along the *a*-axis of the conformers, they concluded a shift of electron density from the side chain into the chromophore during the excitation. By using the analysis outlined for the TDM, we are now also able to discuss the permanent electric dipole moment with respect to the PAS of the chromophore. The angles of the electric dipole moment with the inertial axes of indole and their changes are given in Table 4. Obviously, all changes follow a common pattern; the out-of-plane angle ϕ stays nearly the same, and θ is always rotated by a positive angle.

Very helpful at this point is a work by Kang et al., who presented the electric dipole moments of indole in its ground and electronically excited states.²² They show that excitation to the S₁ diminishes μ slightly from 1.963 D to 1.856 and rotates θ by 12.5° in the same direction as we found in TRP. Therefore, we believe that the rotation of the excited-state dipole moment in all tryptamine conformers is the result of a rotation of the dipole moment in the chromophore and that only little electron migration occurs from the side chain into the ring system as suggested by Nguyen et al.²¹ This can be seen best for the up conformers where the two dipole moments are perpendicular to each other and the values for $\Delta\theta$ come very close to the experimentally determined one for indole.

4. DISCUSSION

Using the above results, we try now to separate the side chain–chromophore interaction into through-space and through-bond effects. According to the large differences in the excitation schemes of the various conformers, the through-space effect seems to dominate the interaction. Nevertheless, if we compare

the excitation scheme of the staggered and eclipsed forms of toluene (Figure 6), we find similar effects as those observed in the different PEA and TRP conformers. (For this molecule, Kroemer et al.² have found a strong angular dependence of the TDM orientation on the methyl dihedral angle.) A strong rotation of the orbitals takes place upon symmetry break, resulting in a rotation of the TDM orientation of 60° for the L_b state (0.7(LUMO ← HOMO)–0.6(LUMO+1 ← HOMO–1)) and of 22° for the L_a state (0.6(LUMO ← HOMO–1)–0.6(LUMO+1 ← HOMO)), indicating the importance of a symmetry break for the changes of the TDM orientation. Such a pronounced non-Condon behavior is quite unexpected and can be traced back to the different hyperconjugative interactions in the staggered and eclipsed forms of toluene. Nevertheless, the TDM orientations over 2 π along the periodic methyl torsional potential for the L_b state average to 90°. For PEA, such vibrational averaging does not take place because the potential energy is not symmetrically periodic. Here, differences in hyperconjugation between the different conformers directly influence the orientation of the TDM. The different hyperconjugative interactions are strong in the HOMO of PEA (cf. Figure 5).

If the main interaction between the ethylamino side chain and the chromophore is through-bond-mediated, the question arises, why the influence of the side chain orientation on the benzene chromophore is much larger than that on the indole chromophore. An explanation of this might be given by the observation that the ionization potentials of ethylbenzene (8.77 eV²³) and ethylamine (8.8 eV²⁴) are practically identical but very different from that of 3-ethylindole (7.5 eV²⁵). This suggests that ionization (and excitation) in TRP is localized in the chromophore, while it is delocalized between the benzene chromophore and the amino group in PEA. This delocalization causes the large sensitivity of the relative amino orientation with respect to the chromophore in the latter.

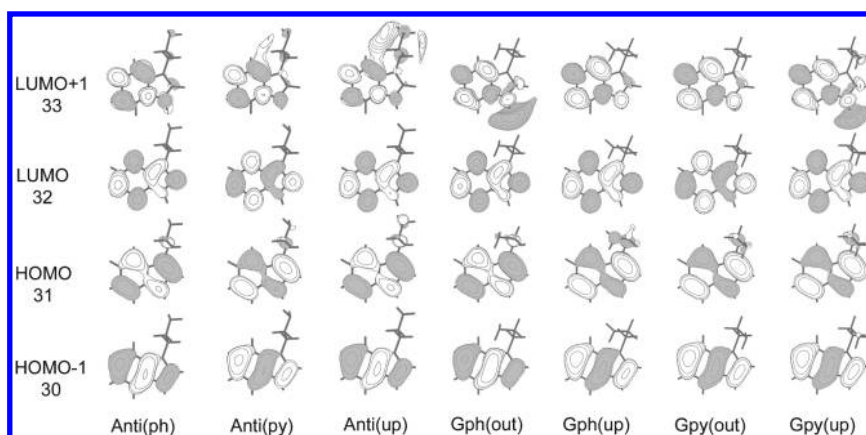


Figure 5. Frontier orbitals of tryptamine involved in an excitation contributing at least 15% of conformers ascertained in beam experiments. An extended picture showing all orbitals of Table 3 and the two in conformers can be found in the Supporting Information.

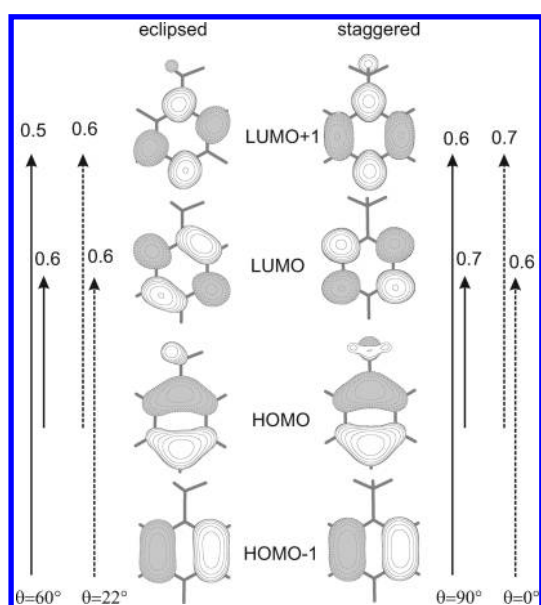


Figure 6. Frontier orbitals and excitation scheme of the staggered and eclipsed forms of toluene. The broken arrows refer to excitation to the L_a state, and the solid arrows are for the L_b state. The numbers on top of the arrows give the coefficient of the respective excitation.

5. CONCLUSIONS

The experimental finding of a large sensitivity of the transition dipole moment for the excitation to the lowest excited singlet state to the conformer structure in phenylethylamine and a much lower sensitivity in tryptamine (indoleethylamine) has been reproduced using DFT/MRCI calculations. The orientation of the TDM of the L_b state in TRP is governed by the chromophore and hardly changes upon geometry changes of the side chain, while its orientation in PEA is governed by the side chain orientation. We trace the large differences in the sensitivity of the TDM orientation on the side chain position back to a delocalized excitation in PEA, while the electronic excitation in TRP is localized in the indole chromophore and experiences only small through-space effects from the amino group. The L_a state TDM orientation stays remarkably constant both in PEA and in TRP. Thus, we have a nearly constant angle between the directions of the L_a and L_b transition dipole moments of 90° , while there are large variations in this angle for PEA. For TRP, it is

immediately obvious why the L_a state TDM orientation does not depend on the amino group orientation; the main single-electron contribution to the excitation is $LUMO \leftarrow HOMO$, both of which are independent of the relative amino position. In PEA however, the L_a state is comprised of nearly equal amounts of $LUMO+1 \leftarrow HOMO$ and $LUMO \leftarrow HOMO-1$. Inspection of the LUMO and LUMO+1 (cf. Figure 3) shows that the rotation of the LUMO is balanced by an opposite rotation of the LUMO+1.

For the gauche conformers of PEA, L_a and L_b states share up to 30% of the single-electron excitations, which reflects a strong mixing of the two states, while in TRP, single-electron excitations can be assigned to one of the excited states exclusively. Coupling of the two lowest excited states of TRP, however, can be induced via Herzberg–Teller coupling through vibrational modes, which resemble the difference vectors of the structures of the two excited states.²⁶ The smaller adiabatic L_a/L_b gap in the case of PEA allows the polar amino group in the gauche conformers to stabilize the polar L_a state so much that it comes into near degeneracy with the L_b state, thus causing state mixing between them.

■ ASSOCIATED CONTENT

S Supporting Information. Frontier orbitals from HOMO–1 to LUMO+3 of the nine most stable tryptamine conformers Gpy(out), Anti(ph), Anti(py), Gph(up), Anti(up), Gpy(up), Gph(out), Gpy(in), and Gph(in). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

This work was supported by the Deutsche Forschungsgemeinschaft through Project SCHM1043/11-1. The authors like to thank the Universitätsrechenzentrum Köln for granted computing time. We thank Rainer Weinkauff, Jörg Tatchen, and Christel Marian for helpful discussions.

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