Charge-Transfer Processes |Hot Paper|

Planarized Intramolecular Charge Transfer: A Concept for Fluorophores with both Large Stokes Shifts and High Fluorescence Quantum Yields

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In memory of Professor Peter Hofmann (12.01.1947–15.08.2015)

Abstract: Fluorophores were successfully used in several areas of chemistry and biochemistry. For many purposes, however, it is necessary that the fluorescence compound features a high fluorescence quantum yield as well as a large Stokes shift. The latter is, for example, achieved by the use of a twisted intramolecular charge-transfer (TICT) compound, which shows a twisted geometry in the excited state. However, the higher the twisting is, the lower becomes in general the fluorescence quantum yield as the resulting emission from the twisted state is forbidden. In order to escape this dilemma, we propose the model of planarized intramolecular charge-transfer (PLICT) states. These com-

pounds are completely twisted in the ground states and planar in the excited states. By means of quantum chemical calculations (time-dependent (TD)-B3LYP and CC2) and experimental studies, we could demonstrate that 1-aminoindole and its derivatives form photoinduced PLICT states. They show both very large Stokes shifts ($\tilde{v}=9000-13500 \text{ cm}^{-1}$, i.e., $\lambda=100-150 \text{ nm}$) and high fluorescence quantum yields. These characteristics and their easy availability starting from the corresponding indoles, make them very attractive for the use as optical switches in various fields of chemistry as well as biological probes.

Introduction

Fluorescence spectroscopy and the closely related areas of phosphorescence spectroscopy have become established and widely employed techniques in analytical chemistry.^[1] They are used in the detection, quantification, identification, and characterization of structures and functions of inorganic and organic molecules as well as biological systems.^[1,2] In search of optical switches we got interested in molecules with large differences between the first absorption and the emission band (Stokes shift). Large Stokes shifts of organic molecules are observed when intramolecular relaxation processes in the excited state lead to an energy minimum, which is removed far away from the initial geometry. If solvent effects are not considered, this

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Supporting information for this article (containing NMR spectra of compounds 8 and 9, Cartesian coordinates, and the absolute energies for all calculated compounds) is available on the WWW under http://dx.doi.org/ 10.1002/chem.201503927. process from the lowest Frank–Condon state to a relaxed adiabatic minimum is called adiabatic photoreaction.

Very large Stokes shifts are observed for compounds for which a twisted intramolecular charge transfer (TICT) occurs by a relaxation in the excited state.^[3,4] The most eminent example is the emission spectrum of 4-(dimethylamino)benzonitrile (DMABN, 1).^[5] Here, besides the "normal" band (B-band), which is due to emission from the ¹L_b state being always present for closely related benzene derivates, there is an additional redshifted band if the spectrum is recorded in polar solvents. This band was assigned to fluorescence from the more polar ¹L_a state and was called "anomalous" emission (A-band). This behavior was interpreted by a model, which assumes that polar solvents permit the rotational isomerization of the substrate (the initially excited state) into the product (the highly polar TICT state) of the electron transfer reaction.^[3,4,6] Meanwhile the intramolecular charge-transfer (ICT) state of DMABN is well characterized^[6b,7-9] and a large number of compounds ranging from symmetric biaryls through organometallic compounds are known, which form TICT states.[3,10]

One important feature of TICT states is their twisted conformation where the two units involved in the charge transfer, that is, the donor D and the acceptor A, are orbitally decoupled.^[3,7] As the fluorescence from the TICT state to the ground state involves two orbitals located on different π systems, which are almost perpendicular to each other, it is overlap forbidden and thus expected to possess a small transition moment. A small TICT fluorescence quantum yield is therefore

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expected. The observed TICT fluorescence occurs mainly from molecules in excited vibrational states.

Here, we intended to design a system, which shows analogous to TICT compounds a rotation of approximately 90° around a single bond in an electronic excited state. This adiabatic relaxation process should lead to a strong Stokes shift. In contrast to the TICT compounds, the emission from the relaxed excited state to the ground state should be allowed. That means, the transition moment and hence, the quantum yield for the observed fluorescence should be high. We assumed that systems meeting the above-mentioned requirements are 1-aminoindole (7) and its derivatives. In the present work, we investigated the fluorescence of some 1-aminoindoles, their corresponding indoles, and the TICT compound DMABN by means of quantum chemical calculations (time-dependent (TD)DFT and CC2). Furthermore, we synthesized the 1-aminoindoles, recorded their fluorescence spectra in different solvents, and compared the experimentally data with the calculated ones.

Results and Discussion

a) Concept

The principle of the formation of different ICT states is depicted in Figure 1. In the case of the planar intramolecular charge-transfer state, the absorption of a photon leads to no essential structural change in the relative orientation of the donor and acceptor groups. Both units are located before and after the intramolecular charge transfer in the same plane. Consequently, the π systems of the subunits are coupled in the ground state as well as in the excited state. The resulting fluorescence is electronically allowed and the observed quantum yield should be high. As no large change in the acceptor group A occurs, the Stokes shift is in general small.



Figure 1. Schematic representation of the change in the geometrical arrangement of the donor groups D and D' as well as the acceptor group A upon going from the ground state to planar ICT (a), TICT (b), and PLICT states (c).

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In most cases of twisted intramolecular charge-transfer compounds, the donor and acceptor moieties are connected by a single bond (Figure 1b). The stabilizing interaction between these units guarantees that both π systems are located in the same plane. The intramolecular charge transfer from the donor D to the acceptor A corresponds to an excitation of one electron from the HOMO to the LUMO. The resulting singlet diradical having one unpaired electron in the HOMO and one electron in the LUMO stabilizes itself by rotation around the single bond. The driving force for the rotation is the minimization of the Coulomb interaction between the two unpaired electrons.^[3] The geometric relaxation results in large Stokes shifts of the TICT fluorescence. However, the rotation also leads to orbitally decoupled π systems of the donor and acceptor systems. As mentioned before, the emission to the ground state is electric-dipole-forbidden, resulting in low to very low fluorescence quantum yields.

Our idea was to combine the positive properties of both (planar ICT and TICT) states to get a system showing large Stokes shifts as well as high fluorescence quantum yields. Our suggestion for such a system is depicted in Figure 1 c. Here, the donor unit D' and the acceptor unit A are rigidly connected in one plane. This feature should guarantee high fluorescence quantum yields. Additionally, the system contains a second donor group D, which is connected to the first donor D' by a single bond. Due to the repulsive interaction between the electron pairs of the donor groups D' and D, they are twisted to each other showing a dihedral angle of about 90°. The absorption of light yields a singlet diradical in which the donor moiety D' has a positive charge. This positive charge can be stabilized by interaction with the free electron pair of the donor group D; that means rotation around the single bond occurs and the resulting state is planar. Accordingly, we call this a planarized intramolecular charge-transfer (PLICT) state. Due to the geometric relaxation in the excited state, the resulting electric-dipole-allowed fluorescence should feature a large Stokes shift. It should be pointed out that this PLICT state is completely different to the planarization of almost planar systems such as the PICT (planar intramolecular chargetransfer) model. This model was used to explain the dual fluorescence of DMABN.^[11] One basic assumption of this PICT model was a planarization of the NMe₂ group in the excited state, which is slightly pyramidalized in the ground state. In contrast to this, the ground state of the PLICT model exhibits two π systems, which are perpendicular to each other and completely orbitally decoupled. Furthermore, the planarization in the excited state takes place by a rotation around a single bond.

b) Investigation of the PLICT states

Systems, which should be able to form a PLICT state, are 1-aminoindole (7) and its derivatives.^[12] The underlying indole 2 is the chromophoric unit of the amino acid tryptophan. Due to its role as a fluorescence marker in biological systems, the fluorescence of indole was intensively investigated.^[13-15] The energy-lowest absorption in the UV spectrum of indole con-



sists of two strongly overlapping bands centered around $\lambda =$ 270 nm. These bands correspond-following the original notation of Platt^{[16]}—to the electronic transitions $S_0 {\rightarrow}^1 L_b$ and $S_0 {\rightarrow}$ ${}^{1}L_{a}$. It should be noted that the terms ${}^{1}L_{b}$ and ${}^{1}L_{a}$ are not based on symmetry arguments for molecules with C_s symmetry such as indole or 1-aminoindole. The labels are only a historic and useful naming convention to specify the lowest excited electronic states of aromatic compounds.^[16] Due to measurements of the electronic absorption spectrum of indole molecules partially oriented in stretched polyethylene host, it is known that the first excited electronic state of indole is the ¹L_b state.^[13c] The ¹L_b state has a dipole moment, which is almost identical to the one of the ground state. This suggests that the ${}^{1}\mathrm{L}_{\mathrm{b}}$ state corresponds to a locally excited (LE) state. Hence, in non-polar solvents the fluorescence of indole occurs from the ¹L_b state.^[13a] In polar solvents, solvent complexes^[17] lower the energy of the strongly dipolar ¹L_a state and the emitting state changes from ${}^{1}L_{b}$ to ${}^{1}L_{a}$.^[13a,b,14a] The strongly dipolar ${}^{1}L_{a}$ state can be considered-within the above-mentioned definition of charge-transfer (CT) states—as planar intramolecular chargetransfer state. The donor unit represents the pyrrole ring and the acceptor unit is the benzene ring of indole.

A substitution of the hydrogen atom of the NH group of indole by an amino group should result in the desired planarized intramolecular charge-transfer compound 1-aminoindole (7). In the electronic ground state the free electron pair of the NH₂ group is almost perpendicular to the π system of the aromatic unit. Upon excitation of the molecule the amino group should rotate around 90° in order to stabilize the positive charge at the nitrogen atom of the pyrrole ring. To support this assumption, we calculated the spectral properties of the 1-aminoindoles 7–11, the corresponding indoles 2–6, and the TICT compound 1 by means of quantum chemical methods

(see Figure 2). Furthermore, we synthesized 1-aminoindole (7) as well as its derivatives 8 and 9 starting from the corresponding indoles 2-4 by an N-amination method according to known procedures.^[12,18] The fluorescence spectra of the indoles 2-4 and 1-aminoindole (7) as well as its derivatives 8 and 9 were recorded in different solvents and compared to the calculated data.

The geometry optimization of the electronic ground states were performed by using Becke's three-parameter hybrid functional (B3LYP^[19]). The geometrical parameters of the excited states were calculated by means of the time-dependent density functional theory (TD-DFT^[20]). It is known that TD-DFT tends to underestimate charge-transfer excitation energies^[21] due to spurious self-interaction.^[22] However, the use of TD-B3LYP yields a good agreement for the vertical excitation energies of the first excited singlet states of TICT compounds, such as DMABN^[23,24] and dialkylaminopyridines.^[25] As basis set the def2-TZVP set was used. Furthermore, the electronic excitation energies of the DFT-optimized structures were computed at the approximate second-order coupled cluster (CC2^[26,27]) levels. Here, again the def2-TZVP^[28] set was used. In exploratory calculations, it was confirmed that a larger basis set with diffuse functions (i.e., def2-TZVPPD) has little effect on the states investigated in this work.

For all compounds 1–11 the ground state and the ¹L_a states, which represent the TICT state (for compound 1), the planar ICT state (for compounds 2–6), and the PLICT state (for compounds 7–11) were optimized. In the case of indole (2) and 1-aminoindole (7) also the excited-state structures of the ¹L_b state were computed (Table 1). Structural parameters of the lowest singlet electronic states (ground, ¹L_b and ¹L_a) of 1-aminoindole (7) calculated by using (TD)DFT are shown in Figure 2b. As expected and found by others,^[29] the ground state



Figure 2. a) Structures of 4-(dimethylamino)benzonitrile (1, DMABN), the indoles 2–6, and the 1-aminoindoles 7–11. b) Structural parameters of the lowest singlet electronic states (ground, ¹L_b and ¹L_a) of 1-aminoindole (7) calculated by using (TD)DFT.

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Table 1. Vertical singlet excitation $(S_0 \rightarrow S_n)$ and emission $(S_0 \leftarrow S_n)$ energies ΔE , Stokes shifts, oscillator strengths (*f*), and permanent dipole moments μ of each state calculated by means of CC2. Furthermore, the main electron configurations from which the transitions arise are also given (H=HOMO, L=LUMO).

	State	μ [D]	Main electron configurations	Transition	Transition energy [cm ⁻¹]	Stokes shift [cm ⁻¹]	f
1	S ₀	7.68		$S_0 \rightarrow L_b$	35 700		0.0326
	¹ L _a (TICT)	15.19	H→L+1	$S_0 \leftarrow L_a$	26800	8900	0.0000001
2	S ₀	2.22		$S_0 \rightarrow L_b$	39 500		0.0283
	¹ L _b (LE)	2.19	H−1→L	$S_0 \leftarrow L_b$	37 500	1900	0.0337
			$H \rightarrow L+2$				
	¹ L _a (ICT)	5.64	$H \rightarrow L$	$S_0 \leftarrow L_a$	36 400	3000	0.1083
3	S ₀	2.38		$S_0 \rightarrow L_b$	39400		0.0306
	¹ L _a (ICT)	4.68	$H \rightarrow L$	$S_0 \leftarrow L_a$	36600	2800	0.1334
4	S ₀	2.32		$S_0 \rightarrow L_a$	38 200		0.1150
	¹ L _a (ICT)	3.27	$H \rightarrow L$	$S_0 \leftarrow L_a$	31 800	6400	0.2016
5	S ₀	6.09		$S_0 \rightarrow L_b$	37 000		0.0441
	¹ L _a (ICT)	10.35	$H \rightarrow L$	$S_0 \leftarrow L_a$	34100	2900	0.1414
6	S ₀	7.21		$S_0 \rightarrow L_b$	38100		0.0111
	¹ L _a (ICT)	11.60	$H \rightarrow L$	$S_0 \leftarrow L_a$	34000	4100	0.0318
7	S ₀	1.88		$S_0 {\rightarrow}^1 L_b$	38 500		0.0451
	¹ L _b (LE)	1.66	$H-1 \rightarrow L$	$S_0 \leftarrow L_b$	37 000	1500	0.0348
			$H \rightarrow L+2$				
	¹ L _a (PLICT)	6.17	$H \rightarrow L$	$S_0 \leftarrow L_a$	28600	9800	0.0516
8	S ₀	2.23		$S_0 \rightarrow L_b$	38600		0.0316
	¹ L _a (PLICT)	5.79	$H \rightarrow L$	$S_0 \leftarrow L_a$	29200	9400	0.0643
9	S ₀	2.28		$S_0 \rightarrow L_a$	36800		0.1206
	¹ L _a (PLICT)	4.28	$H \rightarrow L$	$S_0 \leftarrow L_a$	27 100	9600	0.1729
10	S ₀	4.89		$S_0 \rightarrow L_b$	35 700		0.0764
	¹ L _a (PLICT)	11.34	$H \rightarrow L$	$S_0 \leftarrow L_a$	26000	9700	0.0441
11	S ₀	6.45		$S_0 \rightarrow L_b$	37 500		0.0093
	['] L _a (PLICT)	12.79	$H \rightarrow L$	$S_0 \leftarrow L_a$	27700	9800	0.0272

of compound 7 features a twisted geometry. The dihedral angle $\theta_{\text{(C7a-N-N-H)}}$ amounts to 60° , which means that the free electron pair of the amino group is perpendicular orientated to the π system of the aromatic unit. The same is valid for the 1L_b state. In the case of the 1L_a state, the dihedral angle $\theta_{\text{(C7a-N-N-H)}}$ amounts to -21° allowing a perfect interaction between the free electron pair of the amino group and the aromatic system. Furthermore, the N–N distance is decreased by 0.05 Å going from the optimized S_0 state to the optimized PLICT state 1L_a . Thus, the proposed planarization due to donor⁺–donor interaction upon excitation is validated by the TD-DFT calculations.

According to the CC2 results for 1-aminoindole, the ${}^{1}L_{b}$ state is the first and the ${}^{1}L_{a}$ state is the second excited singlet state if the nuclear positions are fixed at the ground-state structure (vertical excitation). By using the molecular orbital (MO) approximation, the $S_{0} \rightarrow {}^{1}L_{b}$ transition is dominated by an asymmetrical combination of (HOMO-1) \rightarrow LUMO and HOMO \rightarrow (LUMO+2) excitations, whereas the $S_{0} \rightarrow {}^{1}L_{a}$ transition corresponds to the HOMO \rightarrow LUMO excitation. However, this order depends on the substituents. For example, the ${}^{1}L_{a}$ state is the first excited singlet state for 1-amino-3-phenylindole (9). At the excited-state minimum structures of 1-aminoindole, the ${}^{1}L_{a}$ state is the first excited single state. Thus, the fluorescence band corresponds to the $S_{0} \leftarrow {}^{1}L_{a}$ transition.

To visualize how the electron moves when excited, the electron density difference between the ground and excited states of compounds 1 and 7 were calculated by using TD-DFT and are shown in Figure 3. In all cases the isovalues for the surfaces have the same amount. The cyan-colored areas represent the regions where the electron density is reduced upon the excitation, whereas the violet-colored surfaces indicate the areas where the electron density is increased due to excitation. Looking at Figure 3 it becomes obvious that the $S_0 \rightarrow {}^1L_b$ transition for compound 7 leads to a locally excited state showing almost no intramolecular charge transfer. On the other hand, the $S_0 \rightarrow {}^1L_a$ transitions for compounds 1 and 7 cause an intramolecular charge transfer from a donor unit to an acceptor unit. In the case of DMABN (1) the electron density is moved from the NMe₂ group to the benzene ring and to the cyano group. In the case of 1-aminoindole (7) the electron charge is



Figure 3. Transfer of the electron during the excitation from the ground state to the excited state computed by using TD-DFT. In all representations the isovalues for the surfaces have the same amount. The cyan-colored (violet-colored) areas represent the regions where the electron density is reduced (increased) upon excitation. Left) Electron density difference between the ground state and the TICT state of compound 1. Middle) Electron density difference between the ground state and the 'L_b (LE) state of compound **7**. Right) Electron density difference between the ground state and the ¹L_a (PLICT) state of compound **7**.

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transferred upon excitation from the nitrogen atom and the C3 atom of the five-membered ring to the six-membered ring of the indole unit. The intramolecular charge transfer can be confirmed by the increase of the dipole moment. Whereas there is no significant change between the permanent dipole moments of the ground state (1.88 D) and the optimized ${}^{1}L_{b}$ state (1.66 D) for compound **7**, the permanent dipole moment of the ${}^{1}L_{a}$ state of compound **7** amounts to 6.17 D (Table 1). DMABN (1) and 1-amino-5-cyanoindole (11), both featuring an even larger distance between the donor and the acceptor units, have according to the calculations exceedingly high dipole moments of 15.19 and 12.79 D, respectively.

The geometric relaxation from the twisted ground state to the planarized ICT state of compound **7** is caused by a change in the electronic structure upon excitation of the molecule. In order to interpret and explain the planarization in the ICT state of compound **7**, we will consider the frontier orbitals, which are involved in the $S_0 \rightarrow {}^1L_a$ transition of compound **7**. The transition may be described as an excitation of an electron from the HOMO to the LUMO, as is straightforward from the analysis of the calculated transition vectors. In Figure 4 the HOMO and



Figure 4. HOMOs (lower panel) and LUMOs (upper panel) of a) the optimized twisted and b) the planarized (ICT) geometry of 1-aminoindole (7) calculated by using B3LYP.

the LUMO of the optimized twisted (ground state) and the optimized planarized (PLICT state) geometry are shown. A comparison of the LUMOs for both geometries shows that there is no significant change on going from the twisted to the planar structure. The electron, which occupies the LUMO in the excited state, is mainly delocalized over the six-membered ring and the C2 atom of the pyrrole ring. If the HOMOs for both geometries are considered, however, the picture looks rather different. The coefficients at the carbon atoms C4 to C7 decrease on going from the twisted to the planarized structure. The latter geometry shows large coefficients at the two nitrogen atoms and at the C3 atom. The PLICT state of compound **7** may thus be considered as a singlet diradical with one unoccupied electron delocalized within the benzene ring and one unpaired electron delocalized over the two nitrogen atoms and the C3 atom. The driving force for this spatial separation is the minimization of the Coulomb interaction between the two unpaired electrons. However, in contrast to the TICT state of compound 1, the π systems of the two unpaired electrons are still coupled. This is particularly important to ensure that the $S_0 \leftarrow {}^1L_a$ transition is electronically allowed.

To explain the rotation of the amino group upon excitation, we have drawn a qualitative correlation diagram of the HOMOs and LUMOs of the twisted as well as the planarized geometry for 1-aminoindole (7) (Figure 5). As mentioned



Figure 5. Qualitative correlation diagram between the twisted (left) and the planarized (right) geometry of the ground state (S_0) and the excited state 1L_a of 1-aminoindole (7).

before, there is no significant change when going from the twisted to the planar geometry for the LUMO. In the case of the HOMO, planarization leads on one hand to a decrease of the orbital coefficients at the carbon atoms C4 to C7. On the other hand, planarization allows the interaction between the HOMO and the n orbital of the amino group. This leads to a decrease in energy of the bonding linear combination and to an increase of the antibonding linear combination. If both orbitals, the HOMO and the n orbital, are doubly occupied, this interaction is repulsive.^[30] Thus, for the ground state of compound 7 the twisted geometry, where the HOMO and the n orbital are perpendicular to each other, is energetically favored. If the HOMO is only singly occupied, which is the case for the PLICT state of compound 7, the interaction between the HOMO and the n orbital of the amino group represents a three-electron two-orbital interaction, which is in general stabilizing.^[30] Therefore, the planarized structure of the ICT state of compound 7 is energetically favored over the twisted one.



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If we compare the calculated absorption and fluorescence bands of the indoles 2-6 and the 1-aminoindoles 7-11, it can be seen that both the absorption energy and the oscillator strengths for the absorptions do not differ much between the 1-aminoindoles and the corresponding indoles (Table 1). The same is valid for the oscillator strengths of the fluorescence band; thus, both transitions (ICT for indoles and PLICT for 1aminoindoles) are allowed. The oscillator strength of the TICT state of compound 1 is-as mentioned before-almost zero and the observed emission band is due to hot fluorescence from excited vibronic levels. The most obvious difference between the spectral properties of the indoles 2-6 and the 1aminoindoles 7-11 are the Stokes shifts. Whereas the indoles 2-6 feature an energetic difference between the absorption and emission of about $\tilde{\nu} = 3000-6000 \text{ cm}^{-1}$, the Stokes shifts for the 1-aminoindoles **7–11** amount to $\tilde{\nu} = 9500-10\,000 \text{ cm}^{-1}$. The average gap between the indole and corresponding 1aminoindole is more than $\tilde{\nu} = 5500 \text{ cm}^{-1}$.

A comparison between the CC2-computed spectral data (Table 1) and the experimentally observed ones (Table 2) shows a good match between the calculation and the experiment. Furthermore, the experimentally found red shift of the fluorescence of the 1-aminoindoles **7–9** with increasing polarity of the solvent, confirms that the emission occurs from the strongly dipolar PLICT state. The fact that the fluorescence quantum yields of the 1-aminoindoles **7–9** are only slightly dependent on the solvent used, demonstrates that the S₀ \leftarrow ¹L_a transition is electronically allowed. It is known that for an optically forbidden transition the fluorescence quantum yield strongly depends on the solvent polarity.^[24] As an example, the absorption

Table 2. Experimentally determined spectral properties of the indoles 2–4 and the 1-aminoindoles 7–9.								
	Solvent	Absorption	Emi	Emission		Stokes shift		
		λ_{\max} [nm]	[nm]	[cm ⁻¹]	[nm]	[cm ⁻¹]		
2	cyclohexane	261	300	33 300	39	5000	0.464	
	ethyl acetate	269	308	32 500	39	4700	0.593	
	acetonitrile	269	321	31 200	52	6000	0.479	
	methanol	270	330	30 300	60	6700	0.390	
3	cyclohexane	262	301	33 200	39	4900	0.394	
	ethyl acetate	267	303	33000	36	4500	0.340	
	acetonitrile	267	307	32600	40	4900	0.449	
	methanol	267	316	31 600	49	5800	0.298	
4	cyclohexane	263	342	29200	79	8800	0.808	
	ethyl acetate	268	350	28600	82	8700	0.661	
	acetonitrile	269	352	28400	83	8800	0.626	
	methanol	269	356	28 100	87	9100	0.530	
7	cyclohexane	268	357	28000	89	9300	0.505	
	ethyl acetate	273	400	25000	127	11 600	0.177	
	acetonitrile	274	410	24400	136	12100	0.291	
	methanol	272	435	23 000	163	13800	0.241	
8	cyclohexane	267	353	28300	86	9100	0.388	
	ethyl acetate	271	382	26200	111	10700	0.260	
	acetonitrile	271	392	25 500	121	11 400	0.396	
	methanol	271	413	24 200	142	12700	0.135	
9	cyclohexane	262	383	26100	121	12100	0.725	
	ethyl acetate	268	405	24700	137	12600	0.740	
	acetonitrile	268	410	24400	142	12900	0.848	
	methanol	268	425	23 500	157	13800	0.664	

and fluorescence spectra of indole (2) and 1-aminoindole (7) recorded in methanol are shown in Figure 6. Both molecules exhibit similar absorption spectra as the amino group having a free electron pair perpendicular to the aromatic π systems does not influence the vertically excitation. However, the emission band of 1-aminoindole (7) is—as anticipated—strongly red shifted and the Stokes shift amounts to $\tilde{\nu} = 13\,800 \text{ cm}^{-1}$ ($\lambda = 163 \text{ nm}$). Also for the other 1-aminoindoles the Stokes shift has a size of approximately $\tilde{\nu} = 9000-14\,000 \text{ cm}^{-1}$ depending on the solvent used.



Figure 6. Absorption and fluorescence spectra of indole (2) (dashed line) and 1-aminoindole (7) (solid line).

c) LE state versus PLICT state

As mentioned above, the emission spectrum of DMABN (1) shows a dual fluorescence. The normal band arises from emission from the ${}^{1}L_{b}$ state, whereas the red-shifted band is caused by the transition from the TICT (${}^{1}L_{a}$) state to the ground state. Upon vertical excitation, the molecule is transferred from the ground state into the ${}^{1}L_{b}$ state. The latter is in equilibrium with the TICT (${}^{1}L_{a}$) state. The reaction coordinate between these states is the twist angle of the NMe₂ group. By means of TD-B3LYP calculations it could be shown, that the intersection of the ${}^{1}L_{b}$ state and the TICT state occurs at around 52°.^[20] In this area strong vibronic coupling can be expected, which allows for transitions between the two states.

As mentioned before, the LE state (${}^{1}L_{b}$) is the first excited singlet state of 1-aminoindole (**7**) if the nuclear positions are fixed at the ground-state structure. At the excited-state minimum structures of 1-aminoindole, the PLICT (${}^{1}L_{a}$) state is the first excited single state. Therefore, the question arises at which point the LE state and the PLICT state intersect. In order to find this out, we computed the three states (i.e., the ground state, the LE state, and the PLICT state) in dependence on the dihedral angle $\theta_{(C7a-N-N+H)}$. The results are shown in Figure 7. Each point in Figure 7 corresponds to the result of a geometry optimization by means of (TD)B3LYP where all internal degrees of freedom except $\theta_{(C7a-N-N+H)}$ are relaxed. The energies of the states were subsequently computed by using CC2.

A dihedral angle of 60° corresponds to a twisted geometry, whereas the planarized structure has an angle of about -20° .



Figure 7. Computed energy profile for the ground state (solid line), the LE state (dotted line), and the PLICT state (dashed line) of 1-aminoindole (7) in dependence on the dihedral angle $\theta_{\rm (C7a-N-N+H)}$.

A salient feature of Figure 7 is the fact that the PLICT state is independent of the dihedral angle $\theta_{(C7a-N-H)}$ always more stable in energy than the LE state. The energy difference ranges from 2 kcalmol⁻¹ at 60° to 11 kcalmol⁻¹ at -21° . In other words, after excitation of 1-aminoindole (7) into the vibrationally excited LE state, the molecule can transform into the PLICT state at any value of $\theta_{(C7a-N-H)}$. This explains the fact that no dual fluorescence is found for 1-aminoindole (7) (Figure 6). The fluorescence always occurs from the PLICT state. This behavior makes the 1-aminoindoles even more attractive for the usage as optical switches as there is a large gap between the absorption and the emission band.

Conclusion

In sum, we could show by means of quantum chemical calculations (TD-B3LYP and CC2) that 1-aminoindole (7) and its derivatives form photoinduced planarized intramolecular chargetransfer states. These states differ basically from the TICT states, as the intramolecular charge transfer does not cause a twisting of a planar system, but a planarization of a twisted system by rotation around a single bond. Even more important is the fact that the emission band from the PLICT states is allowed, whereas the fluorescence arising from the TICT states is optically forbidden. The experimentally determined absorption and fluorescence spectra of 1-aminoindole (7) and its derivatives confirm the quantum chemical predictions. As 1-aminoindoles can be easily synthesized in large amounts starting from the corresponding indoles,^[31] they are highly promising fluorophores. They show very large Stokes shifts (>100 nm) as well as high fluorescence quantum yields, which makes them attractive for the use as optical switches and as biological probes.

Experimental Section

Computational details: All calculations were performed by using the program package TURBOMOLE.^[32] The geometrical parameters of the stationary points were optimized by means of $\mathsf{B3LYP}^{\scriptscriptstyle[19]}$ for the electronically ground state and by TD-B3LYP^[20] for the excited states. The def2-TZVP^[28] basis set was employed. The ground states and the ¹L_a states were optimized for all compounds. In the case of indole (2) and 1-aminoindole (7) also the optimized excited-state structures of the ¹L_b states were calculated. For all stationary points no symmetry restrictions were applied. Frequency calculations were carried out at each of the structures to verify the nature of the stationary points. All optimized states have none imaginary frequency. Furthermore, the energies, the electronic excitation energies, the permanent dipole moments, and the oscillator strengths for the transitions were computed at the approximate second-order coupled cluster (CC2^[26,27]) levels on the DFT-optimized structures. Here, again def2-TZVP^[28] was used. By exploratory calculations it was confirmed that a larger basis set with diffuse functions (def2-TZVPPD) has little effect on the states investigated in this work.

In order to calculate the energy in dependence on the dihedral angle $\theta_{(C7a-N-N-H)'}$ all three states (i.e., the ground state, the LE state, and the PLICT state) of 1-aminoindole (7) were optimized by means of (TD)B3LYP/def2-TZVP, whereby all internal degrees of freedom except $\theta_{(C7a-N-N-H)}$ were relaxed. The energies of the states were subsequently calculated by using CC2/def2-TZVP.

General remarks: All chemicals were reagent grade and were used as purchased. Reactions were monitored by TLC analysis with silica gel 60 F254 thin-layer plates. Flash chromatography was carried out on silica gel 60 (230–400 mesh). ¹H and ¹³C NMR spectra were recorded on a 600 MHz spectrometer. All chemical shifts (δ) are given in [ppm]. The spectra were referenced to the peak for the protium impurity in the deuterated solvents indicated in brackets in the analytical data. High-resolution mass spectra were recorded by using a time of flight (TOF) detector. 1-Aminoindole (**7**) was synthesized according to a known procedure.^[18]

1-Amino-7-methylindole (8): To a vigorously stirred suspension of indole 3 (1.52 g, 11.6 mmol) and KOH (13.6 g, 242 mmol) in DMF (40 mL), NH_2OSO_3H (4.85 g, 42.9 mmol) was added at 0°C under an argon atmosphere. After 3 h stirring at room temperature, water was added to the solution and the residue was filtered. The filtrate was extracted three times with toluene. The combined organic phases were dried over MgSO₄ and the solvent was removed under vacuum. The crude product was purified by column chromatography over silica gel (methylene dichloride) to yield compound 8 as a white solid (204 mg, 1.40 mmol, 12%). M.p. 109.1-109.2°C; ¹H NMR (600 MHz, [D₆]DMSO): $\delta = 7.29$ (d, ³J(H,H) = 7.7 Hz, 1 H; H_{ar}), 7.14 (d, ${}^{3}J(H,H) = 3.1$ Hz, 1H; H_{ar}), 6.83 (d, ${}^{3}J(H,H) = 7.2$ Hz, 1H; H_{ar}), 6.78 (d, ${}^{3}J(H,H) = 7.0$ Hz, 1H; H_{ar}), 6.23 (d, ${}^{3}J(H,H) = 3.1$ Hz, 1H; H_{ar}), 6.07 (s, 2H; NH_2), 2.77 ppm (s, 3H; CH_3); ^{13}C NMR (151 MHz, $[D_6]DMSO$): $\delta = 134.15$, 130.90, 126.42, 123.21, 121.06, 118.72, 118.18, 97.46, 18.54 ppm; IR (ATR): $\tilde{\nu} = 3346$, 3043, 3018, 2965, 2866, 1905, 1835, 1767, 1621, 1579, 1516, 1481, 1456, 1423, 1379, 1344, 1320, 1293, 1248, 1199, 1160, 1112, 1102, 1077, 1049, 1037, 963, 887, 838, 779, 747, 711 cm⁻¹; HRMS (ESI+): *m/z* calcd for C₉H₁₀N₂+Na⁺: 147.0922; found: 147.0917.

1-Amino-3-phenylindole (9): To a suspension of indole **4** (193 mg, 1.00 mmol) and KOH (1.17 g, 20.9 mmol) in DMF (5 mL), NH_2OSO_3H (418 mg, 3.70 mmol) was added at 0 °C under an argon atmosphere. After 24 h stirring at room temperature, water and methylene chloride were added to the solution. The phases were separated and the aqueous phase was extracted several times with meth-



ylene chloride. The combined organic layers were dried over MgSO₄ and the solvent was removed under vacuum. The crude product was purified by column chromatography over silica gel (ethyl acetate/*n*-hexane 1:2) to yield compound **9** as a beige solid (80 mg, 0.38 mmol, 38%). M.p 100.4–101.2 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.96 (d, ³*J*(H,H) = 8.0 Hz, 11; H_{ar}), 7.67 (dd, ³*J*(H,H) = 7.9 Hz, ⁴*J*(H,H) = 1.1 Hz, 2H; H_{ar}), 7.46 (t, ³*J*(H,H) = 8.1 Hz, 3H; H_{ar}), 7.35 (s, 1H; H_{ar}), 7.34–7.29 (m, 2H; H_{ar}), 7.22 (td, ³*J*(H,H) = 7.7, ⁴*J*(H,H) = 0.9 Hz, 11; H_{ar}), 4.53 ppm (s, 2H; NH₂); ¹³C NMR (151 MHz, CDCl₃): δ = 137.39, 135.27, 128.75, 127.36, 127.04, 125.85, 124.24, 122.29, 120.30, 119.88, 114.70, 108.67 ppm; IR (ATR): $\tilde{\nu}$ = 3318, 3255, 3195, 3107, 3053, 1603, 1534, 1492, 1459, 1359, 1328, 1259, 1216, 1184, 1158, 1134, 1075, 1030, 1013, 956, 919, 819, 763, 739, 690, 657 cm⁻¹; HRMS (ESI+): *m/z* calcd for C₁₄H₁₂N₂+Na⁺: 231.0898; found: 231.0917.

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