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Spectroscopic and Theoretical Studies of 6-*N*,*N*-Dimethyladenine[†]

Andreas B. J. Parusel,[‡] Wolfgang Rettig,[§] and Krystyna Rotkiewicz*,[∥,⊥]

*Institute of Theoretical Chemistry and Structural Biology, University of Vienna, Rennweg 95b,
A-1030 Vienna, Austria, Institut für Chemie, Fach-Institut für Physikalische und Theoretische Chemie,
Humboldt-Universität zu Berlin, Taylor-Str. 2, D-12489 Berlin, Germany, Institute of Physical Chemistry,
Polish Academy of Sciences, Kasprzaka 44, PL-01−224 Warsaw, Poland, and Institute of Chemistry,
Świętokrzyska Academy, Chęcińska 5, PL-25-020 Kielce, Poland*

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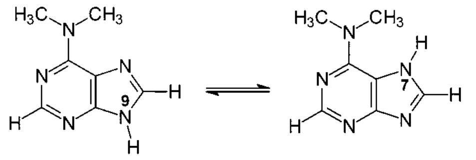
In contrast to adenine, *N*,*N*-dimethylated adenine (6-*N*,*N*-dimethyladenine, DMADE) emits dual fluorescence in solvents of different polarity. The low energy band has been ascribed to emission from an intramolecular charge transfer (TICT) state, the high energy B band to a locally excited state localized mostly within the purine ring. The low-temperature measurements of the fluorescence of DMADE, as well as of that of 6-*N*,*N*-dimethyladenosine indicate that the 9H tautomer of DMADE is the main emitting species of this compound. The precursor−successor B → A model in the kinetic range describes the emissive properties of DMADE at room temperature even in weakly polar solvents. The effective deactivation process, characteristic for nucleic acid bases, competes with the transformation to the ICT state. Theoretical computations are in good agreement with the experimental results.

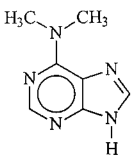
Introduction

The photophysical properties of adenine (ADE), one of the nucleic acid bases, have attracted the attention of scientists since four decades. The aim of these studies was mainly a better insight into UV-induced genetic damage. The quantum yield of the fluorescence of adenine (3×10^{-4}), as well as for other nucleic acid bases is very low.[1,2] Probably, the evolution has selected the material showing minimal emittivity and short excited state lifetime to reduce the photoreactions in the living cell. ADE can exist in two main tautomers, the 9H and the 7H form, but it exists in the ground state mainly as the 9H tautomer.[3,4] However, the major part of the emission of ADE derives from the 7H tautomer[5,4] (cf. Scheme 1 for *N*,*N*-dimethylated adenine, DMADE). The relative concentration of the 7H tautomer was reported as 6%[5] or 22% in aqueous solution.[4] The quantum yield of ADE fluorescence (mainly from the 7H tautomer) increases in low-temperature alcohol glasses.[4]

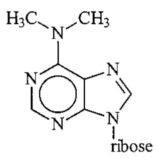
SCHEME 1



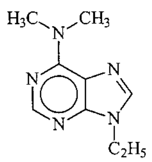
Adenine is attached in DNA similarly as the other nucleic acid bases to the phosphate backbone through a ribose at 9 position.[6,7] Recently, Albinsson reported the results of photophysical investigations of adenosine (ADO) and its *N*,*N*-dimethylated derivatives. In adenosine, a ribose moiety is attached in position 9 to the adenine backbone and thus excludes the existence of the tautomer 7H (Formulas).



DMADE



DMADO



DM9EA

Alkylation of the amino group of adenosine (DMADO) results in an anhancement of its emissive properties. Moreover, in contrast to ADO a dual fluorescence consisting of distinctly separated bands is observed.[6,7] The low energy A band has been ascribed to emission from an intramolecular charge transfer (ICT) or twisted ICT (TICT) state, the high energy B band to a locally excited state mostly ascribable to the purine rings. The B fluorescence of 6-*N*,*N*-dimethyl-9-ethyladenine (DM9EA) showed a very low quantum yield of the order of 10^{-4}, i.e., comparable with that of the ADE 7H tautomer, although DM9EA exists only as 9H tautomer. The quantum yield of the A fluorescence is about 10 times larger,[7] i.e., of the order of magnitude 10^{-3}. The dual fluorescence of DMADO showed some similarities to that of TICT forming DMABN (4-(*N*,*N*-dimethylamino)benzonitrile). These similarities [6,7,8] were related to the following: (i) small radiative rates of the CT fluorescence

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* To whom correspondence should be addressed. Fax: +4839120238. E-mail: krysiar@ichf.edu.pl.

[‡] Institute of Theoretical Chemistry and Structural Biology, University of Vienna.

[§] Institut für Chemie, Fach-Institut für Physikalische und Theoretische Chemie.

[∥] Institute of Physical Chemistry, Polish Academy of Sciences.

[⊥] Institute of Chemistry, Świętokrzyska Academy, Chęcińska 5, PL-25-020 Kielce, Poland.

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of 10^{-6} s^{-1}, (ii) blue shift of the A band correlated with the change of the oxidation potential of different alkylated amino groups as donors, (iii) sensitivity to the twist angle of the donor around the C−N bond, (iv) quenching of the A band in protic solvents, (v) character of the temperature dependence of both bands. However, some differences must be noticed. They concern the magnitude of the dipole moment in the CT state and the magnitude of the charge transfer. The experimentally estimated dipole moment of 6-*N*,*N*-dimethyl-9-ethyladenine (DM9EA) in the CT state is 9.5 D only, about 2 D more than that of the ground state, whereas the dipole moment of the DMABN in the TICT state is not smaller than 13 D.[9] The calculations lead to the value of 5.8 D for the former molecule in the CT state and indicate that the moments in CT and ground state are almost perpendicular to each other. Thus, the solvent shift is large, but the charge separation cannot be full in DM9EA.[7] Recently, on the basis of the investigations of the dual fluorescence kinetics of DMADO and its derivatives, a model was proposed in which the A and B state are formed rapidly from a common FC state, and there is no mother-daughter relationship between them,[7] although the precursor−successor ($B^* \rightarrow A^*$) relationship was reported previously by Albinsson.[6]

The investigation of the photophysics of 6-*N*,*N*-dimethyladenine (DMADE) was the object of our studies. This compound can exist, similarly as adenine, at least as two tautomers: 9H and 7H, although the amount of the latter could be very small due to steric hindrance, introduced by the methylation of the amino group. DMADE is composed of both an electron donor (the *N*,*N*-dimethylamino group) and an electron acceptor subunit (purine). The aim of our study has been to find an answer to the following questions: (i) does DMADE also emit dual fluorescence? (ii) from which isomer does fluorescence occur, is it the same as in the case of adenine where mainly the tautomer 7H is the emitting one? (iii) what is the nature of the emitting states? (iv) does proton transfer occur from possible dimers in nonpolar solvents or in complexes with protic solvent molecules? Theoretical computations were performed and the results compared with experimental ones.

Experimental Section

Compounds: DMADE (6-dimethylaminopurine, 98%, Aldrich Chem. Co) and DMADO (6-dimethylaminopurine-9-riboside, Sigma) were used as received. The solvents were of spectral grade. The absorption spectra were recorded either on Carl Zeiss 500 spectrophotometer or an ATI UNICAM UV4 UV/VIS one. Corrected emission spectra of DMADE were measured with a Perkin−Elmer MPF3 spectrofluorimeter and in the case of DMADE and DMADO in butyl chloride at low temperatures they were obtained on an SLM-Aminco Bowman AB2 spectrofluorimeter. The fluorescence quantum yields at 298 K were measured relative to quinine bisulfate in 0.1 N H_2SO_4 ($\phi_F = 0.51$)[10] and are corrected for the refractive index of the solvents. The quantum yield of DMADE fluorescence in methylene chloride and acetonitrile solutions were measured relative to known comparable fluorescence yields of DMABN: 0.046[11] and 0.036[12] (the values corresponding to air saturated conditions) in the same solvents, respectively.

Temperature dependent fluorescence spectra were measured with a homemade cooling apparatus that allows simultaneous freeze and control of the temperature of four samples in quartz cuvettes by pumping cold nitrogen gas through the cryostat.

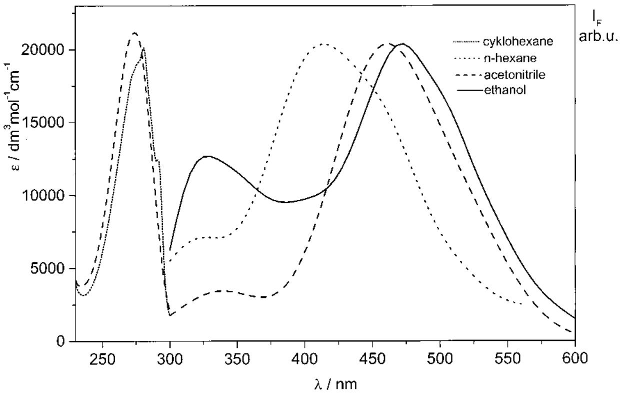


Figure 1. Absorption and fluorescence spectra of DMADE at room temperature.

Computational Methods

Semiempirical calculations are performed with the VAMP program package, version 7.0[13] using the standard AM1[14] Hamiltonian. All geometries are optimized in the electronic ground state and no restrictions in geometry are assumed. The excited-state geometries are optimized employing the configuration interaction scheme with single and double excitations (CISD) with an active space of 10 orbitals, corresponding to 876 configurations used in the configuration interaction (C. I.). For solute−solvent interactions the self-consistent reaction field (SCRF)[15] is applied. Acetonitrile is chosen as an example of a highly polar but aprotic solvent. Additional geometries are optimized by variation of both the twist angle θ in steps of 15° and the pyramidalization angle ω in steps of 5°. Both angles characterize the dimethylamino group of DMADE with the twist angle θ defined as half the dihedral angle $\{\varphi(C_2-C_1-N-C') - \varphi(C_{2'}\text{-}C_1-N-C'')\}/2$ (for numeration of atoms, see Scheme 1) and the pyramidalization angle ω as the angle between the plane formed by the dimethylamino unit and the purine plane, respectively.

Results and Discussion

The absorption and fluorescence spectra of DMADE in differently polar solvents are depicted in Figure 1.

The absorption spectra show a slight blue shift with increasing solvent polarity and the fluorescence spectra are composed of two bands. In addition to a normal fluorescence (B) at ca. 330 nm, a second solvent polarity sensitive band (A) is observed in the long wavelength range (430 nm-460 nm) in dependence on polarity, Figure 1. The fluorescence spectra closely resemble those of DMADO and its derivatives, as reported by Albinson et al..[6,7] The transition energies, as well as the ratio of the relative intensities of both bands are very similar for the two compounds. Moreover the quantum yields of the fluorescence and measured decay times are very close in the same solvents at room temperature (Table 1). The radiative lifetimes of the DMADE fluorescence, calculated from the quantum yields and measured decay times data are rather long, i.e., of the magnitude order of several hundreds ns, showing on the strongly forbidden character of the emitting ICT state.

The fluorescing adenosines as studied in[6] correspond to the 9H tautomer of adenine due to blocked tautomerisation by substitution in the 9-position. On the basis of the close similarity of the DMADE emission to that of DMADO the conclusion may be drawn that the emission of DMADE most probably occurs from the 9H-tautomer, contrary to the case of adenine, emitting out of tautomer 7H (see Introduction).

TABLE 1: Spectral Characteristic of the Fluorescence of DMADE and DMADO

compd	solvent	$\nu(F_B)$/ cm^{-1}	$\nu(F_A)$/ cm^{-1}	Φ (F_A)	$\tau(F_A)$/ns^a
DMADE	Cyclohexane		23300		1.3
	Tetrahydrofurane		22400		1.9
	Buthyl chloride		22700	2×10^{-3}	2.0
	CH_2Cl_2		22300	5×10^{-3}	
	Acetonitrile	30100	21800	2.5×10^{-3}	1.1
	Ethanol	30300	21300		
DMADO	Acetonitrile		19600	1.5×10^{-3}	0.7

[a] The decay times were measured by Dr. Karl Rechthaler at maximum of the long wavelength A-band, i.e., below 500 nm.[17] Albinsson observed short growing in at A-band of DMADO at wavelength larger than 500 nm.[6]

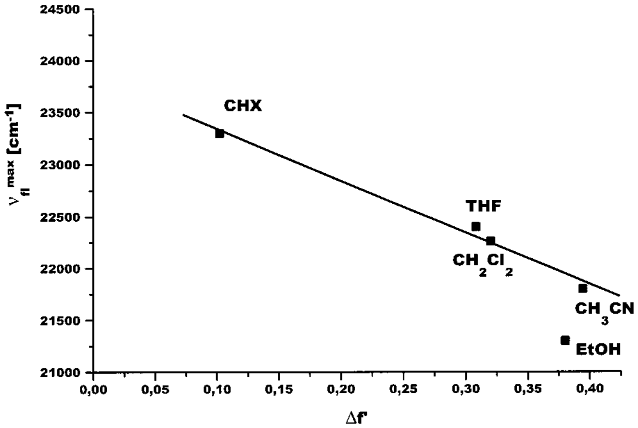


Figure 2. Lippert−Mataga plot for the A-fluorescence band maxima vs the polarity function Δf.

The Lippert−Mataga plot, drawn for the maxima of the A fluorescence band, is presented in Figure 2.

The large solvent shift of the A band suggests a remarkable CT character of the emitting state. From the Lippert−Mataga relation (Figure 2) the product $\mu_A(\mu_A - \mu_g) = 58.5$ D^2 was obtained, assuming an Onsager radius equal to 500 pm. The value obtained from theoretical calculations for the product of value of the dipole moment in A-state and vectorial difference of dipole moments in A-state and ground state is very similar, namely 54.5 D^2 and 54.6 D^2 for the 9H and 7H forms, respectively. The solvatochromic shift in alcohols is larger than in aprotic solvents of the same polarity. This effect was observed in the case of DMADO,[6,7] too. The hydrogen bonding on one of the purine ring N atoms possibly enhances the acceptor strength for the formation of the A state as well as the CT character of the emitting state.

Albinsson has given two different photophysical models for DMADO. According to ref 6, the transformation from the B- to the A-state occurs at room temperature in the kinetic region (i.e., irreversibly), and it is a thermally activated process with an Arrhenius activation energy of the order of magnitude 2 kcal/mol. Nonradiative deactivation of DMADO should occur exclusively through A-state at room temperature. The important evidence for this model was the rise time of the A-fluorescence in the subnanosecond time region.

In ref 7 the second possible model was reported: the A- and B-states should be formed rapidly from a common FC state, and they could not interconvert. In this branching model, both states therefore decay independently, i.e., there is no precussor-successor relationship between them. This conclusion was supported by the lack of a growing in of the A-fluorescence for 6-*N*,*N*-dimethyl-9-ethyladenine, which shows a very similar dual fluorescence to that of DMADO and similarly as DMADO cannot exist as 7H tautomer.

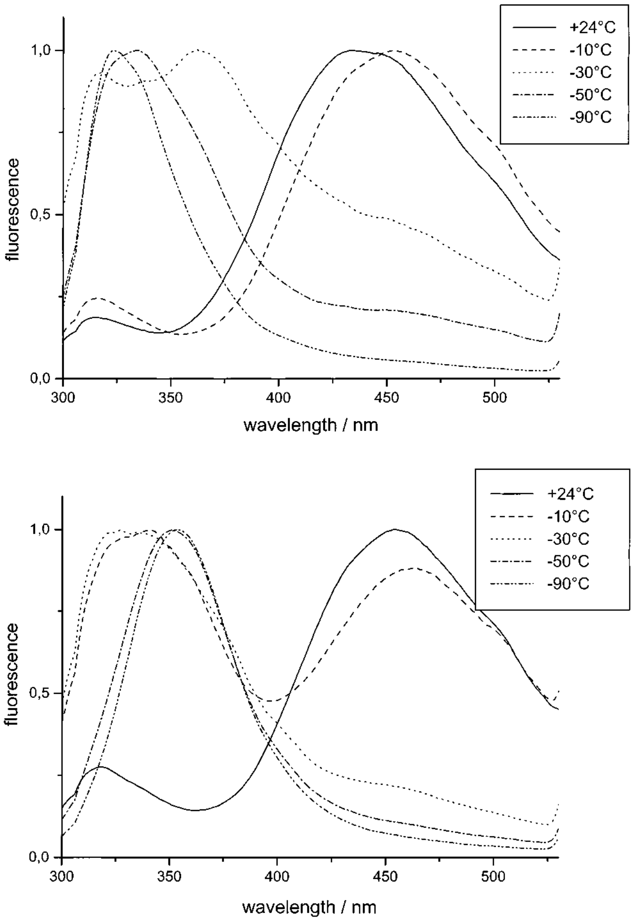


Figure 3. (a) Temperature dependence of the DMADE fluorescence in butyl chloride (297−183 K); (b) This dependence for DMADO.

Low-temperature studies can bring additional evidence here, because the precursor−successor model and the branching model are expected to yield different temperature dependences. We therefore performed measurements of the fluorescence spectra of DMADE in solution of butyl chloride at temperatures between 297 K and 153 K. The normalized spectra in this temperature region are depicted in Figure 3.

The intensity of the A band decreases upon decreasing the temperature from 297 K, whereas the B-band increases remarkably when the temperature decreases down to 203 K.

Below this temperature, its relative intensity practically does not change. This is exemplified for DMADE in Figure 4.

Such a behavior is typical for the kinetic regime of a precursor−successor model, i.e., for an irreversible process k_{BA} of A-state formation at low temperatures competing with the decay of the precursor (B) state. This occurs below some characteristic temperature T_2 when k_{BA} becomes smaller than k_B (rate constant of the deactivation of the B-state).[16] This model is identical to a model developed for TICT state formation,[16] Scheme 2. Consistent with this model, a near constancy of the A-band relative intensity is observed between 297 and 273 K and its decrease below that temperature, where the B-band begins to increase considerably, indicating the onset of the critical temperature T_2. The changes of the logarithm of the quantum yield with $1/T$ for both bands of DMADE fluorescence correspond to the same Arrhenius energy about 5 kcal/mol. For

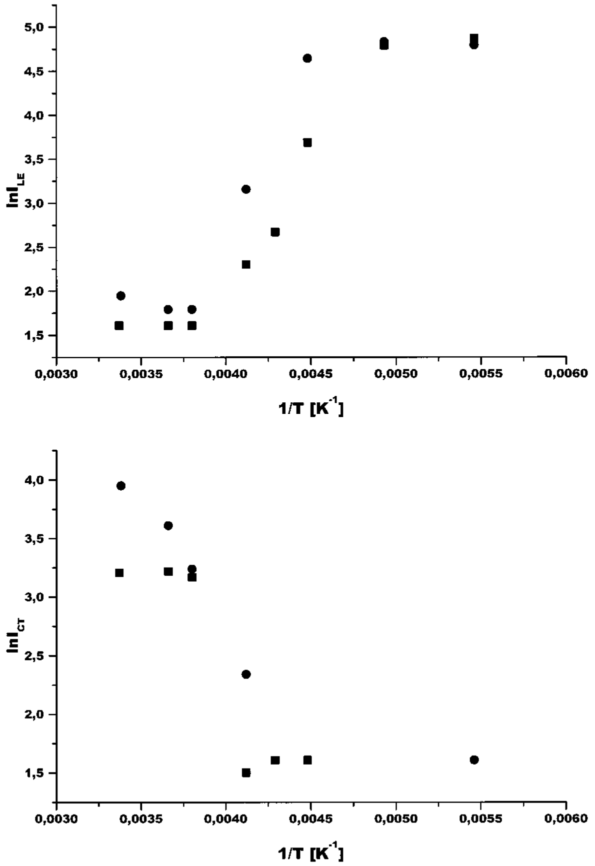
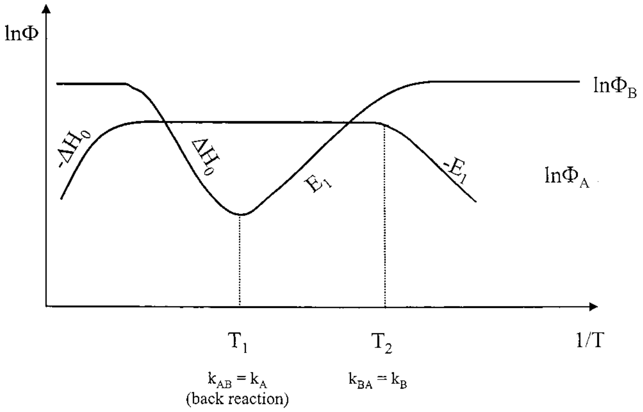


Figure 4. Logarithm of the fluorescence quantum yield, approximated by the band intensities, of: (a) LE and (b) CT fluorescence bands of DMADE in *n*-butyl chloride as a function of inverse temperature. The squares and circles correspond to a DMADE concentration of 2.9 × 10^{-5} M and 5.8 × 10^{-5} M, respectively.

SCHEME 2



DMADO with weaker solubility in *n*-butyl chloride, the activation energy could only be very rougly estimated to 3 < E_a < 10 kcal/mol.

Thus, we can conclude for both compounds that the simple photophysical model B* → A* is the most probable one (Scheme 3). The critical temperature T_2 of equal size for the k_{BA} and k_B rate constants occurs here at much higher temperature than in the case of DMABN due to the more effective radiationless deactivation of the B-state in nucleic acid bases.

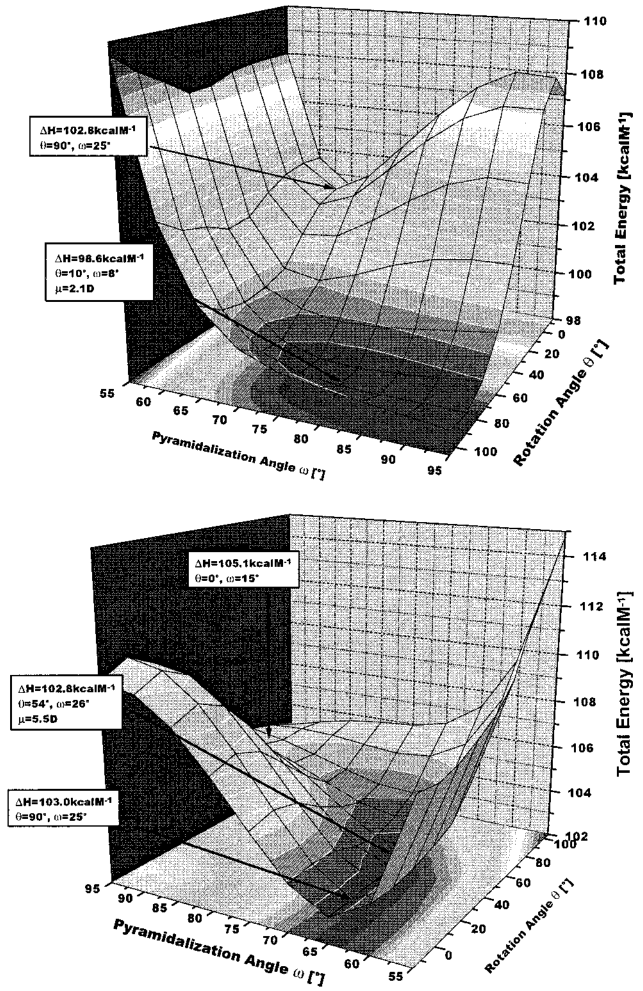
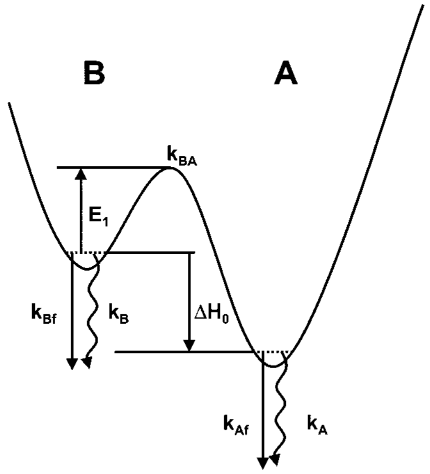


Figure 5. Ground-state energy surfaces of 9H-DMADE and 7H-DMADE as a function of the rotation angle θ and pyramidalisation angle ω.

SCHEME 3



Some fluorescence spectra depicted in Figure 3 show shoulders and hint to the presence of further fluorescens species, e.g., for DMADE at 243 K. These additional bands, in the short wavelength region, are rather small in comparison with the B-band observed at 183 K and may be due to different conformers or different solute–solvent complexes forming at low temperature.

Computational Results

Ground State. The ground state energy surface of 9H-DMADE and 7H-DMADE are shown in Figure 5 as a function of both the twist angle θ and the pyramidalization angle ω

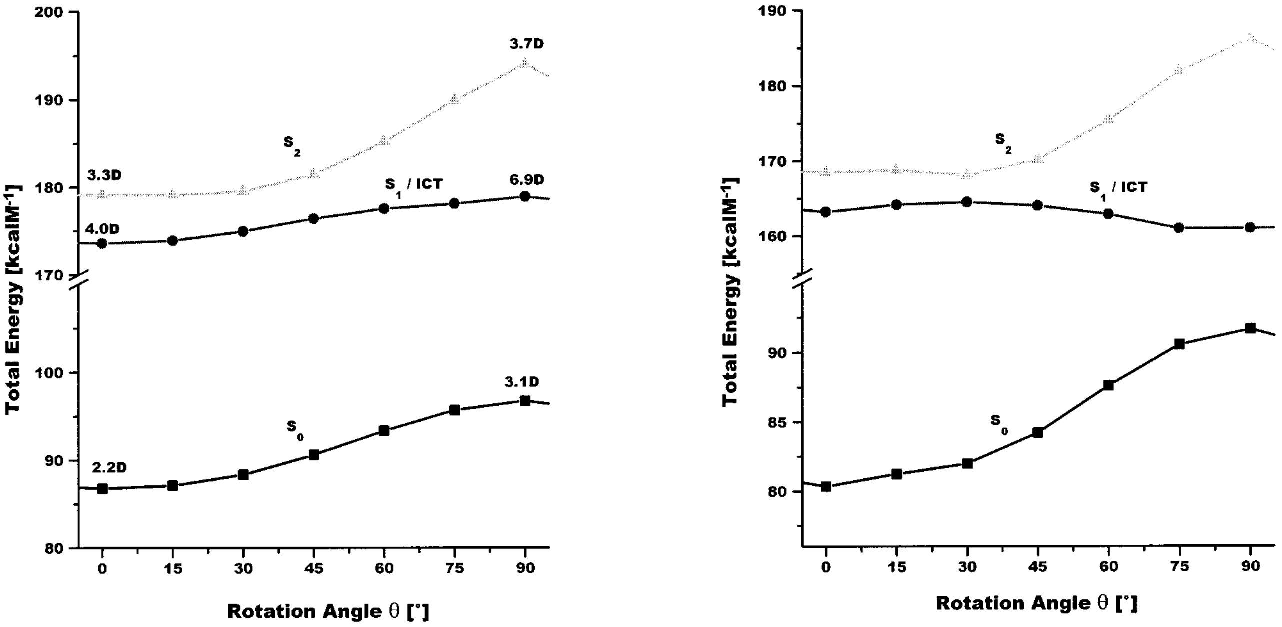


Figure 6. Dependence of the total energy of the 9H-DMADE on the rotation twist angle *θ* in gas phase (a, left), and in acetonitrile, (b, right).

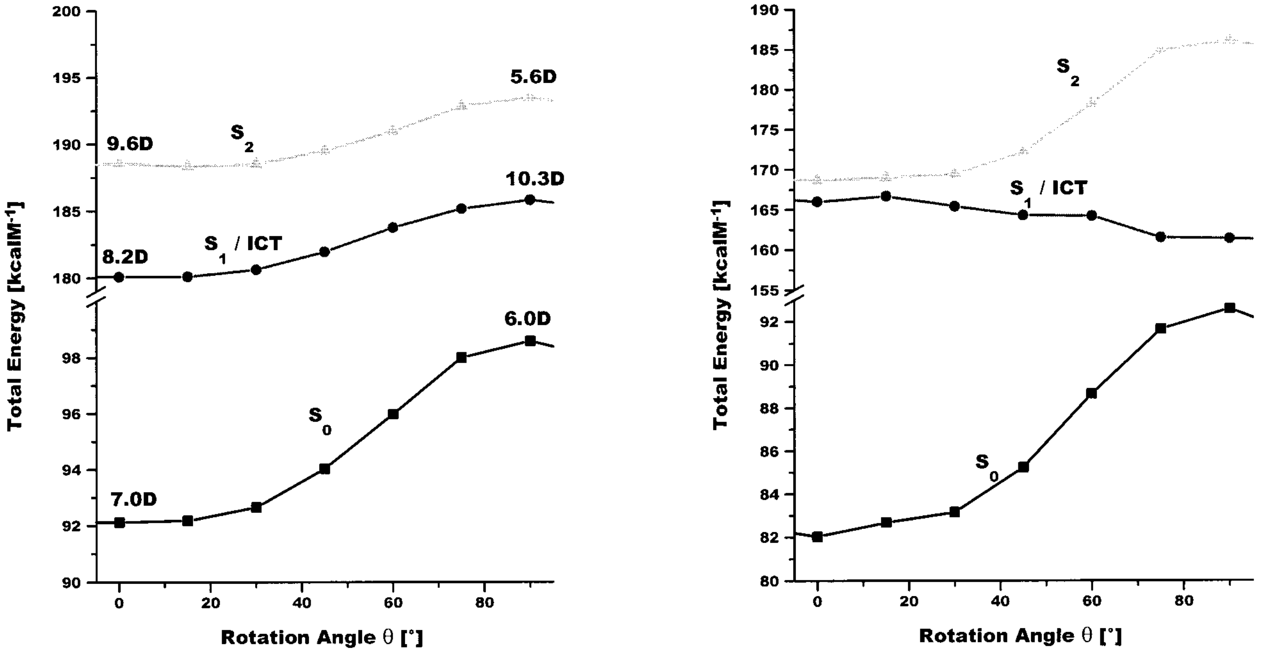


Figure 7. Dependence of the total energy of the 7H-DMADE on the rotation twist angle *θ* in gas phase (a, left), and in acetonitrile, (b, right).

TABLE 2: Ground State Properties of DMADE with Δ*H* Energy (in kcal/mol), ΔΔH Rotation Barrier (in kcal/mol), *μ* Dipole Moment (in D), *θ* Rotation Angle (in °), *ω* Pyramidalization Angle (in °) of the Dimethylamino Group

	Δ*H*	ΔΔ*H*	*μ*	*θ*	*ω*
9H-DMADE	98.6	4.2	2.1	10°	8°
7H-DMADE	102.8	2.3/0.2[a]	5.5	54°	26°

[a] Energy Barrier for Planarization

(Table 2). The lowest energy conformation of both tautomers is computed to be at different geometries. The energy of the 9H-DMADE optimized geometry of Δ*H* = 98.6 kcal/mol is more stable by 4.2kcal/mol than the 7H-DMADE tautomer (Δ*H* = 102.8 kcal/mol) corresponding to a relative ground state population at room temperature of ca. 99,9%:0.1% for the two tautomers. 9H-DMADE is most stable in the conformation with the dimethyl amino group twisted out of the purine plane by 10°. The rotation barrier is calculated to only 4.2 kcal/mol, which is sufficiently small so that also more twisted conformations can be populated in the electronic ground state. The slightly pyramidal amino nitrogen of 9-DMADE ($\omega = 8°$) increases its inversion angle along the rotation coordinate where the twisted ($\theta = 90°$) ground state structure has a pyramidalization angle *ω* of 25°. In 7H-DMADE, the most stable conformer is twisted by 54° (with $\omega = 26°$) and separated only by 2.3 kcal/mol from the completely twisted conformer with $\theta = 90°$ and $\omega = 25°$. The untwisted conformation ($\theta = 0°$ and $\omega = 15°$) is 2.3 kcal/mol higher in energy compared to the 7H-DMADE ground state minimum. The small rotation barriers in the electronic ground state allow the population of the excited FC state also from significantly twisted geometries in both the 9H- and 7H-DMADE systems.

Excited States. The first excited states of both tautomers are optimized. The resulting structure is more planar relative to the ground-state structure: 9H-DMADE has a planar untwisted and nonpyramidal dimethylamino group at 173.6kcal/mol ($\mu = 4.0$D) with $\theta = 0°$ and $\omega = 0°$ and 7H-DMADE is slightly twisted with $\theta = 17°$ and $\omega = 12°$ with an energy of 179.8 kcal/mol ($\mu = 6.4$D). The first excited state of 9H-DMADE (7H-DMADE) is characterized mainly by a HOMO→LUMO transition (55% for 9H-DMADE and 53% for 7H-DMADE) and a HOMO→LUMO+1 transition. The S_2 on the contrary is mainly of HOMO→LUMO+1 (43% for 9H-DMADE and 69% for 7H-DMADE) and by a minor contribution of HOMO→LUMO character. The HOMO is of π bonding character within the purine ring with a small π^* character at the carbon−nitrogen single bond. Both the LUMO and the LUMO+1 are π^* antibonding MO's in the purine ring. Both the S_1 and the S_2 are thus characterized mainly by a $\pi\pi^*$ transition within the aromatic subsystem with a minor electron shift from the amino nitrogen to the purine unit.

At decoupled conformation, the first excited state of both tautomers is mainly of HOMO→LUMO character (79% for 9H-DMADE and 69% for 7H-DMADE). Here, the HOMO is described best as a free electron pair at the amino nitrogen decoupled electronically from the aromatic unit by a 90° twist angle. The LUMO is partly of $\pi^*_{\text{(purine)}}$ character. Thus, the S_1 at $\theta = 90°$ represents the TICT state with a large dipole moment of 6.9D for 9H-DMADE and 10.3D for 7H-DMADE. The analysis of the first and second excited state at ground-state geometry of both tautomers identifies no significant differences. Also at $\theta = 90°$ both tautomers form a TICT state with a dipole moment significantly larger that the S_1 dipole moment at $\theta = 0°$. Also, the character of the frontier molecular orbitals is comparable for both molecules. Differences arise due to the different rotation angle for 9H-DMADE and 7H-DMADE in the electronic ground state, which is $\theta = 10°$ for 9H-DMADE and $\theta = 54°$ for 7H-DMADE.

With increasing the twist angle the energy of the first excited state increases for both 9H-DMADE and 7H-DMADE. The rotation barrier is of comparable size for both tautomers: 5.3 kcal/mol for 9H-DMADE and 6.4 kcal/mol for 7H-DMADE. Also the increase of the excited-state dipole moment of ca. 3D−4D is of comparable size. The optimized TICT state (i.e., $\theta = 90°$ and $\omega = 0°$) represents a saddle point on the S_1 energy surface for both systems with the maximum in dipole moment of 6.9D for 9H-DMADE and 10.3D for 7H-DMADE (Figure 6, 7). The large dipole moment of the TICT state causes a significant stabilization in energy in polar solvents. The calculations with acetonitrile as a polar aprotic solvent yield two minima on the first excited-state energy hyper-surface for both tautomers. Both the less polar planar S_1 state and the polar TICT state become a minimum in energy with the TICT state more stable compared to the planar S_1 state minimum ($\Delta\Delta H_{9\text{H}-\text{DMADE}} = -2.2$kcal/mol, $\Delta\Delta H_{7\text{H}-\text{DMADE}} = -4.8$kcal/mol). The barrier separating both conformers is relatively small for both tautomers, 1.3 kcal/mol for 9H-DMADE and 0.7kcal/mol for 7H-DMADE (Table 3).

The results of the theoretical computations confirm the experimental evidence: (i) the transition energies in the fluorescence spectrum of the dominating 9H-DMADE tautomers are in satisfactory agreement with the calculated values: 30100 and 28 900 cm^{-1} for the B-band and 21 800 and 24 300 cm^{-1} for the A-band, respectively; (ii) the lowest singlet excited state of 9H-DMADE in polar solvents has TICT character; (iii) the experimental value for the product of $\mu_A(\mu_A - \mu_g)$ is the same as the calculated number within experimental uncertainty; (iv) the same order of magnitude is found for the activation barrier: the experimental value is ca. 5 kcal/mol in butyl chloride and 1.3 kcal/mol in acetonitrile according to the semiempirical computations.

TABLE 3: Calculated Excited State Properties of DMADE with $\Delta\Delta H_{Barr}$ Rotation Barrier (in kcal/mol), $\Delta\Delta H_{min}$ Energy Difference ΔH_{TICT}-ΔH_{LE} (in kcal/mol) in Gas Phase and Acetonitrile, μ_{LE} the Dipole Moment of the Locally Excited State (in D), μ_{TICT} the TICT State Dipole Moment (in D), α the Angle (in °) between $\mu_0(\theta{=}90°)$ and μ_{TICT}, and μ_{ICT}(exp) the Experimental ICT State Dipole Moment (this work)

	gas phase		solvent (CH_3CN)					
	$\Delta\Delta H_{barr}$	$\Delta\Delta H_{min}$	$\Delta\Delta H_{barr}$	$\Delta\Delta H_{min}$	μ_{LE}	μ_{TICT}	α	μ_{ICT}(exp)[a]
9H-DMADE	+5.3	+5.3	+1.2	−2.2	4.0	6.9	117	5−8
7H-DMADE	+5.8	+6.4	+0.7	−4.8	6.4	10.3	22	9−11

[a] With the following assumption: Onsager radius varying from 4 Å to 5 Å; the value for μ_0 and the angle between μ_0 and μ_{TICT} is taken from the calculations

Summary

The *N*,*N*-dimethylated derivative of adenine, i.e., DMADE shows dual fluorescence, present in solvents of different polarity. It originates from a primary excited state and a relaxed excited state. The relaxed excited state is of polar character with the dimethylamino group twisted about the C−N single bond, i.e., it corresponds to a TICT state. This conclusion is drawn from the similarity of the emission properties to those of 6-*N*,*N*-methylated-adenosine (DMADO), the fluorescence of which was investigated and interpreted by Albinsson,[6,7] as well as from the similarity to the emission behavior of the classic TICT forming DMABN. The comparison of the fluorescence behavior of DMADE and DMADO, especially based on the results of our low-temperature measurements hint on the 9H tautomer as the main emitting form of DMADE. Moreover, these results lead to the conclusion that the simple B → A precursor−successor photophysical model in the kinetic range describes very well the kinetics of the excited states of DMADE, contradicting the branching model recently reported by Andreasson et al..[7] According to our model the effective nonradiative deactivation process of the B state competes with the relaxation to the A (TICT) state. Both rate constants become equal at a temperature of about 253 K. The theoretical calculations support the experimental results. They corroborate the TICT nature of the long wavelength emitting state including its highly polar and weekly emissive nature.

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References and Notes

(1) Callis, P. R. *Annu. Rev. Phys. Chem.* **1983**, *34*, 329.
(2) Fletcher, A. N. *J. Mol. Spectrosc.* **1967**, *23*, 221.
(3) Longworth, J. W.; Rahn, R. O.; Shulman, R. G. *J. Chem. Phys.* **1966**, *45*, 2930.
(4) Wilson, R. W.; Callis, P. R. *Photochem. Photobiol.* **1974**, *20*, 345.
(5) Eastman, J. W. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *75*, 407.
(6) Albinson, B. *J. Am. Chem. Soc.* **1997**, *119*, 6369.

(7) Andreasson, J.; Holmen, A.; Albinsson, B. *J. Phys. Chem. B* **1999**, *103*, 9782.

(8) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim* **1979**, *3*, 443.

(9) Baumann, W.; Bischof, H.; Fröhling, J. C.; Brittinger, C.; Rettig, W.; Rotkiewicz, K. *J. Photochem. Photobiol. A: Chem* **1992**, *64*, 49.

(10) (a) Meech, S. R.; Phillips, D., *J. Photochem.* **1983**, *23*, 193; (b) Velapoldi, R. A., Epstein, M. S. *ACS Symp. Series* **1989,** *383*, 98.

(11) Rotkiewicz, K.; Köhler, G. *J. Luminesc.* **1987**, *37*, 219.

(12) Rotkiewicz, K.; Grabowski, Z. R.; Jasny, J. *Chem. Phys.* Lett. **1975**, *34*, 55.

(13) Rauhut, G.; Alex, A.; Chandrasekhar, J.; Steinke, T.; Sauer, W.; Beck, B.; Hutter, M.; Gedeck, P.; Clark, T. VAMP7.0, Oxford Molecular Ltd., Oxford, 1998.

(14) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

(15) G. Rauhut, T. Clark, T. Steinke, *J. Am. Chem. Soc.* **1993**, *115*, 9174−9181.

(16) Grabowski, Z. R.; Rotkiewicz, K.; Rubaszewska, W.; Kirkor−Kamińska, E. *Acta Phys. Polon*. **1987**, *A54/6*, 767.

(17) The A-fluorescence lifetimes were measured by Dr. Karl Rechthaler