Correlated Rotations and Unusual Fluorescence Properties of *peri*-Substituted, Axially Chiral Naphthyl Ketones

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The dynamics of the two rotors in 8-(dimethylamino)naphthyl ketones possessing a tetrahedral amino group and a trigonal planar carbonyl group has been investigated by ^{1}H NMR spectroscopy. The dynamic system is described by an aryl–nitrogen and an aryl–carbonyl rotation and a possible amine inversion. As the two rotors, which are twisted in the ground state, are tightly interlocked, the question arises of how strongly the processes might be correlated and how strongly the electrostatic interactions would influence the barriers. In the case of the isopropyl, *tert*-butyl, and benzyl ketones, the rotors are coupled sufficiently strongly that correlated rotations become energetically preferred over independent rotations of the individual groups. For the methyl and trimethoxyphenyl ketone, the Ar–N and Ar–C barriers could be distinguished because of the lesser degree of interlocking of the substituents. The low barriers and the similar Ar–C and Ar–N rotations, despite the differences in substituents, are due to the pseudo-rotation and inversion of the tetrahedral NMe_2 group. Such a process dramatically reduces the steric and electrostatic hindrance in the transition state and also lessens an energetically costly twist of the naphthalene plane. The larger steric hindrance of a complete inversion partly compensates for the weaker electrostatic repulsion, and so a trigonal-planar transition state is suggested. This additionally allows larger *peri* distances. The 1,8-donor/acceptor-substituted naphthalenes showed unusual fluorescence properties; increases in solvent polarity led to large anomalous Stokes shifts and to a decrease in fluorescence. Methyl 8-(dimethylamino)naphthalene-1-carboxylate produced an anomalous Stokes shift of $\Delta\tilde{\nu}$ = 18354 cm^{-1}.

Introduction

"Molecular gears" or "propellers" have mainly been designed from the aspect of whether two or three rotors produce a correlated or noncorrelated motion.[1,2] Generally, in *ortho*-substituted benzenes and *ortho*- or *peri*-substituted naphthalenes, the barriers of rotation are high when the two rotors are planar, intermediate when one group is tetrahedral and one planar, and low when both substituents are tetrahedral.[3]

Barriers of rotation about the aryl−nitrogen and aryl−carbonyl bonds have been studied in 1-(dialkylamino)-benzene-2-carboxy compounds.[4] An uncorrelated dynamic process was found for the system with the less voluminous bromine atom in the 3-position, whereas a strongly correlated process was found for the corresponding *tert*-butyl system, where the two rotors are more tightly interlocked. Correlated rotations about Ar−C and N−CO amide bonds were also found for axially chiral, tertiary aromatic amides.[5,6] The amino group in the planar amide becomes pyramidal in the transition state. In this way, steric hindrance with neighboring groups is strongly reduced. Even in the case of axially chiral thioamides of acrylic acids, correlated rotations were found between the N−CS thioamide bond and the =C−C= alkenyl carbonyl bond.[7]

While much work has been done for amides, less is known about axially chiral, aromatic ketones. Hindered 1-naphthyl ketones with a methyl group in the 2-position adopted − in the ground state − twisted conformations almost exactly orthogonal to the naphthalene plane, and this resulted in enantiomerization barriers of 33−84 kJ/mol.[8] An Ar−C barrier of 49.8 kJ/mol was determined for the *peri*-substituted 1-benzoyl-8-benzylnaphthalene.[9]

The barriers of rotation in hindered aromatic amines are considered to be independent of the inversion process,[10] because N-inversions in aromatic amines have very small barriers (*N*-methylaniline: N-inversion = 6.7 kJ/mol, N-rotation = 30.3 kJ/mol).[11] However, a benzyl and methoxy substituent dramatically increased the inversion barrier in *N*-benzyl-*O*,*N*-dimethylhydroxylamine, for which a barrier of 53.9 kJ/mol was found in *n*-hexane and 39.3 kJ/mol in dichloromethane.[12] Correlated processes of N-inversions and -rotations were found for *N*-*tert*-alkybenzylamines[13] and for other acyclic nitrogen compounds.[14]

This work investigates structure-barrier correlations, the dynamic processes, and the properties of 1,8-DA-substituted naphthalenes with tetrahedral donors and trigonal-planar acceptors (Figure 1), because in their crystal structures they showed unusual details due to donor−acceptor interactions. X-ray structure analyses[15−17] showed that the distance between the *peri* substituents is larger with A−A

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substitution (ca. 300 pm) and decreases with D−A substitution (ca. 250 pm). With A−A or D−D substitution, both groups are pushed outward from the *peri* area against H^2 and H^7 because of electrostatic repulsion. With D−A substitution, the donor is turned inward into the *peri* area, due to the electrostatic attraction towards the acceptor, which is pushed outward against H^2 (Figure 2).[15] The D−A distance decreases with increasing strength of donor and acceptor groups: ketones < esters < amides. All movable *peri* substituents are twisted out of the naphthalene plane and may form interconvertible enantiomers[4] (Figure 3). The two rotor groups are in direct contact, because no solvation sphere separates the substituents, and the distance between the substituents is smaller than the sum of their van der Waals radii. Therefore, the strong noncovalent interactions force the substituents and the aromatic skeleton to change bond lengths and bond angles. A nonplanar orientation, relative to the naphthalene plane, of the substituents in *peri*-substituted naphthyl ketones and carboxamides was also shown by a combination of Kerr effect and dipole moment methods.[18]

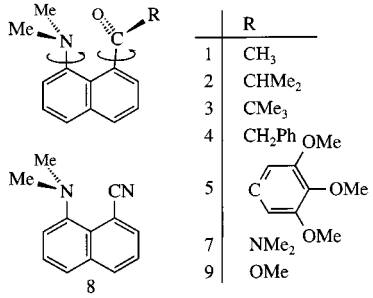


Figure 1. Ketones **1**−**5** and reference compounds

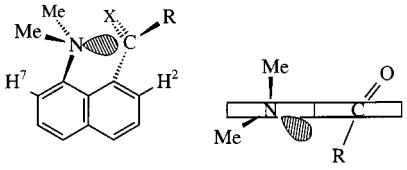


Figure 2. Distortion of the substituents of 1,8-donor/acceptor-substituted naphthalenes in the crystal structure;[15] the exocyclic bonds are displaced above and below the naphthalene plane and the rotors are perpendicular to the main plane; the donor (nucleophile) is splayed inward into the *peri* area towards the acceptor (electrophile), which in turn is pushed outward against H^2; the NMe_2 group is pyramidal and the free electron pair is directed towards the carbon atom of the carbonyl group because of the repulsion of the free electrons at the oxygen atom; the carbonyl plane is small, but significantly distorted by electrostatic interactions; this has been called a "frozen" state of the beginning of a nucleophile addition to a carbonyl group

This raises key questions. How does the electrostatic interaction influence the rotation barriers? Are the rotors coupled strongly enough that correlated rotations will be preferred energetically over independent rotations of the individual groups? Hence, the *peri*-substituted naphthyl ketones **1**−**5** were studied (Figure 2).

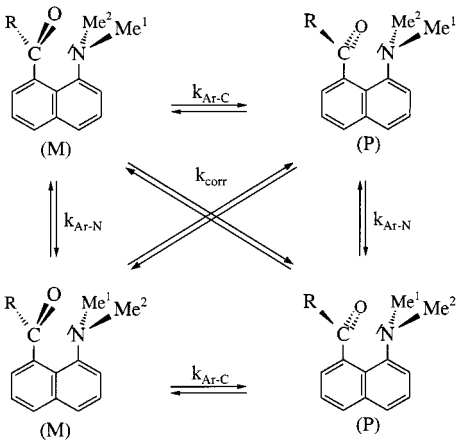


Figure 3. Definition of the enantiomers *M* and *P* and the dynamics in the *peri*-substituted naphthyl ketones; the rotation about the Ar−C bond corresponds to an interconversion of the two enantiomers, owing to the restricted rotation about the naphthalene−carbonyl bond; the term k_{Ar-C} is the rate constant for the Ar−C rotation, k_{corr} the rate constant for correlated processes

Results and Discussion

Barriers of Rotation

In 8-(dimethylamino)-1-naphthyl ketones, there are three different motions: two rotations about the Ar−N and Ar−C bonds, and a possible inversion of the tetrahedral amino group. The Ar−C rotation corresponds to an interconversion of the *M* and *P* enantiomers, arising from the restricted rotation about the naphthalene−carbonyl bond (Figure 3). The barriers were determined by dynamic ^1H NMR spectroscopy, using the coalescence method. Only in cases where the barriers were very different was it possible to distinguish the Ar−N and Ar−C rotations.

The coalescence of the NMe_2 signals cannot automatically be assigned to the Ar−N rotation (Table 1), because it describes only the faster of two processes, and so may also represent the Ar−C rotation. In the presence of optically active (+)-(*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol, the NMR signals of the racemic ketones split, due to the newly formed diastereomeric associates. In this way, it was possible to determine the Ar−C barriers in the methyl ketone **1** and the trimethoxyphenyl ketone **5**, because the coalescence of $NMe^{(M)}$ $Me^{(P)}$ of the diastereotopic NMe_2 groups clearly describes the Ar−C rotation (Figure 4 and Figure 5). But from the coalescence experiments, only a lower limit of the activation enthalpy could be determined, because it was difficult to distinguish between a clear coalescence and an overlap of the signals.

The barriers (Table 1) with and without optically active auxiliary differ by only 6.7 and 8.5 kJ/mol for the methyl ketone **1** and by only 2.4 kJ/mol for the trimethoxyphenyl ketone **5**. To make sure that the higher barriers are not due to the complexation with the auxiliary, the experiment with the methyl ketone **1** was repeated with a racemic auxiliary (Figure 5). This complexation raised the barrier by only 0.5 and 2.3 kJ/mol; therefore, the barrier of > 66.1 kJ/mol for

Table 1. Rotation barriers $\Delta G^{\ddagger}$ of 1-acyl-8-(dimethylamino)naphthalenes; $\Delta\nu_c$: ^{1}H NMR shift differences, extrapolated to the coalescence temperature T_c; ν_o: ^{1}H NMR transmitter frequency; (+)-A: (+)-(*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol

	R	Solvent	Aux.	$T_c \pm 3$ [°C]	k_c s^{-1}	$\Delta G^{\ddagger}$ [kJ/mol]	Rotation	Signals used	$\Delta\nu_c$ [Hz]	ν_o [MHz]
1	Me	$CDCl_3$	–	25	234.1	59.4 ± 0.6	Ar–N	NMe^1Me^2	107.4	250
		CD_2Cl_2	–	0	55.8	57.6 ± 0.8	Ar–N	NMe^1Me^2	26.0	60
		CD_2Cl_2	(±)-A	29	264.1	59.9 ± 0.5	Ar–N	(MP)–NMe^1Me^2	124.0	250
		CD_2Cl_2	(+)-A	13	5.1	≥ 66.1	Ar–C	(MP)–NMe^1Me^2	3.6	250
2	$CHMe^1Me^2$	CD_2Cl_2	–	37	80.3	64.7 ± 0.7	Ar–N/Ar–C	NMe_1Me_2	37.0	80
		CD_2Cl_2	–	31	54.8	64.4 ± 0.7	Ar–C	$CHMe^{1/2}$	25.1	80
3	CMe_3	$Cl_2CDCDCl_2$	–	109	83.3	80.3 ± 0.6	Ar–N/Ar–C	NMe^1Me^2	38.4	80
		CD_2Cl_2	–	<< −85	–	<< 40	C–CMe_3	C–CMe_3	[a]	80
4	CH_2Ph	CD_2Cl_2	–	20	82.8	61.0 ± 0.6	Ar–N/Ar–C	NMe^1Me^2	38.3	80
		CD_2Cl_2	–	11	45.4	60.4 ± 0.7	Ar–C	CH_AH_BPh	11.5	80
5	TriMP[b]	$Cl_2CDCDCl_2$	–	67	46.6	72.8 ± 0.7	Ar–N	NMe^1Me^2	22.2	80
		CD_2Cl_2	–	−68	132.6	41.2 ± 0.7	Ph–C		60.0	80
		$Cl_2CDCDCl_2$	(+)-A	71	27.5	≥ 75.2	Ar–C	(MP)–NMe^1Me^2	22.9	250

[a] ^{1}H NMR shift difference assumed for the calculation of an upper limit of $\Delta G^{\ddagger}$. – [b] TriMP: 3,4,5-trimethoxyphenyl. – [c]CH_3O groups in 3- and in 5-position of the 3,4,5-trimethoxyphenyl substituent.

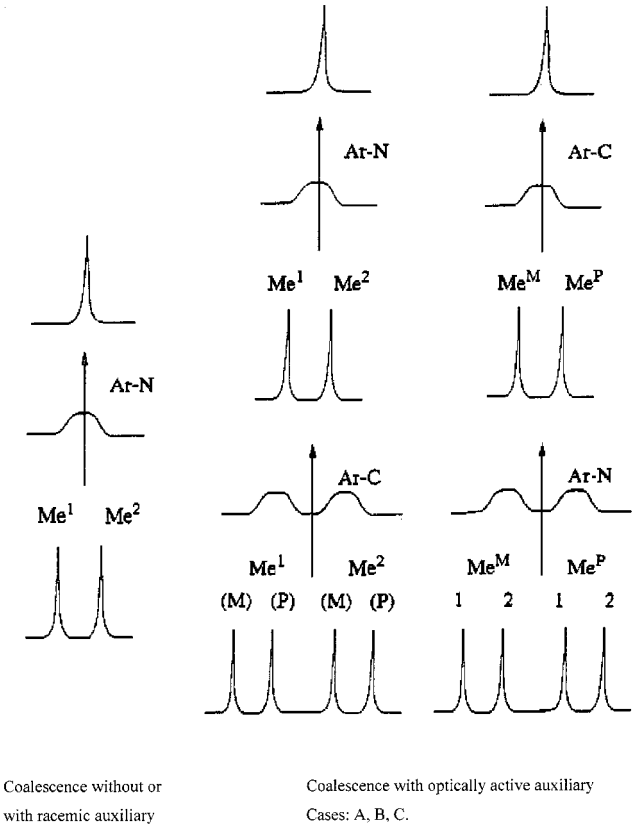


Figure 4. Idealized description of ^{1}H NMR coalescence experiments with and without optically active auxiliary, to differentiate between Ar–N and Ar–C rotations; A: Ar–N >> Ar–C: Ar–C rotation is determined; B: Ar–N << Ar–C: Ar–N rotation is determined; C: Ar–N ≈ Ar–C: theoretically both barriers can be measured, but in practice either the one around Ar–N or the one about Ar–C is obtained; a differentiation is only possible with exact knowledge of $\Delta\nu$, or if the rotations have sufficiently different barriers

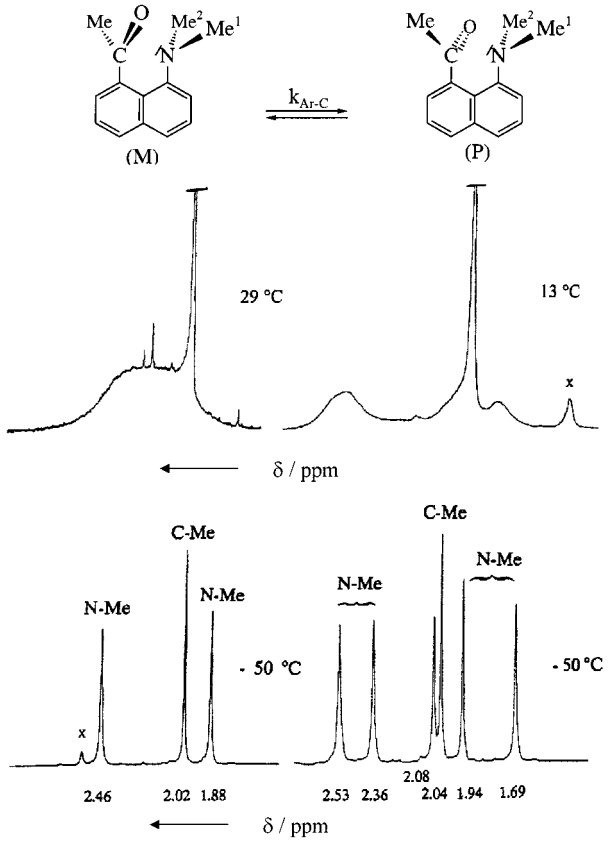


Figure 5. The NMe_2 signals of methyl ketone **1** with racemic (left) and optically pure (+)-(*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol (right); the signals are split with the optically pure auxiliary, but no additional signals are observed with the racemic auxiliary because of the optically inactive medium; x: H_2O impurity

methyl ketone **1** and that of 75.2 kJ/mol for trimethoxyphenyl ketone **5** can be assigned to the Ar–C rotation, and the different barriers measured by the coalescence of the NMe_2 signals without auxiliary (59.4 kJ/mol and 57.6 kJ/mol for **1**, 72.8 kJ/mol for **5**) can be assigned to the Ar–N rotation. However, the assignment for ketone **5** has to be undertaken with care, because the difference of 2.4 kJ/mol between the Ar–C and Ar–N rotations is very small. This indicates that "gear slipping" by pseudo-rotation and inversion of the tetrahedral amino group is possible. The barrier of 41.2 kJ/mol arrived at from the coalescence of the *meta*-OMe groups of the phenyl ring is due to the hindrance of the phenyl–C rotation.

In the isopropyl ketone **2** (64.4 kJ/mol) and the benzyl ketone **4** (60.4 kJ/mol), the coalescences of the signals of the diastereotopic methyl groups and the methylene H atoms (appeared as an AB system) clearly describe the Ar−C rotation (Table 1). The coalescence of the NMe_2 signals, however, resulted in barriers for isopropyl ketone **2** (64.7 kJ/mol) and for benzyl ketone **4** (61.0 kJ/mol) that were almost identical to the barriers determined for the Ar−C rotations. For assignment of these we have to consider three cases. In the first case, the barriers might be equal by accident. We can rule this out, because in the case of the very similar methyl ketone **1** we could determine different barriers. In the second case, the Ar−C rotation would be the faster process; therefore the NMe_2 coalescence would describe this process. In this case it is not possible to assign the barriers inferred from the NMe_2 coalescence to the Ar−N rotation. In the third case, a strongly correlated process would make it impossible to distinguish between the two barriers. This case would require a careful structure−barrier correlation. If we were to increase the steric hindrance of the methyl ketone **1** by introducing isopropyl and benzyl groups, the Ar−C barrier should increase. However, on the contrary, the barriers decrease in the ketones **2** and **4**. This can only be explained by the assumption that synchronous, strongly correlated rotations are preferred over independent rotations of the individual groups. The barriers measured for **2** and **4** represent, therefore, a strongly correlated Ar−C and Ar−N rotation. In the case of *tert*-butyl ketone **3**, assignment of the NMe_2 coalescence to a particular rotation was not possible, because no information about the Ar−C rotation could be obtained, even at −85 °C. However, considering the results from ketones **2** and **4**, we have to assume that correlated rotations are preferred because of the high steric strain. This is also shown in the large increase of the barrier for **3**, by 15.6 kJ/mol compared to the isopropyl ketone **2**.

Transition States

The rotations in these molecules are hindered sterically and electronically. It is not possible to treat both effects separately, because they influence each other. The rotors are desolvated and in direct contact; therefore, the colliding substituents do not have many possible options to keep their distance from one another to reduce the strains. But small changes in bond lengths and angles of the exocyclic bonds and in the $C^1C^2C^3$ *peri* range (Figure 6) can effect a relatively large relaxation of the steric strain. Therefore, small barriers were measured for 1,8-diarylnaphthalenes (68.6 kJ/mol),[19] although rotation was hardly possible on models.

The barriers for the methyl ketone **1** and the isopropyl ketone **2** are about 32 and 20 kJ/mol higher than those for the 2-methylnaphthyl ketones (methyl ketone: 33.9 kJ/mol, isopropyl ketone: 44.7 kJ/mol),[8] which would be accounted for by the higher steric hindrance of the *peri* position. However, the *tert*-butyl ketone **3** (80.3 kJ/mol) has a very similar barrier to that of the *tert*-butyl 2-methyl-1-naphthyl ketone[8] (83.6 kJ/mol). One would expect a much higher barrier for **3**, due to the larger steric hindrance and the additional electrostatic interaction. Additionally, the much larger amide group, compared to that in ketone **3**, in 8-(dimethylamino)-1-(dimethylcarbamoyl)naphthalene raised the barrier by just 16.6 kJ/mol for Ar−C and 8.7 kJ/mol for Ar−N [for 8-(dimethylamino)-1-(dimethylcarbamoyl)naphthalene a barrier of 71.6 kJ/mol was determined for the Ar−N rotation by NMR, and 96.9 kJ/mol for Ar−C rotation by thermal racemization].[20] This shows that the steric hindrance is not strictly additive with regard to the barriers of rotation and that electrostatic interactions have large influences.

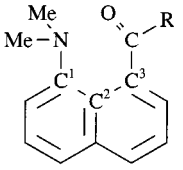


Figure 6. Small bond and angle changes in the *peri* area cause large changes at the substituents

The interpretation of these results requires a closer look at the transition states and the rotation mechanisms. Whereas, in amides, the pyramidal ground state of the *peri*-(dimethylamino) group is stabilized because of the amide dipole, the electrostatic repulsion from the electron pairs at the oxygen atom destabilizes the tetrahedral ground state of the amino group of the ketones (Figure 7a).[15,18] The rotation of the carbonyl group from the ground state of the *M* enantiomer (GS^M) into the *peri* area (TS^1) increases the electrostatic repulsion between the free electron pairs at the amino and carbonyl groups (Figure 7b). Subsequent inversion of the amino group reduces the electrostatic repulsion at the cost of a higher steric hindrance of Me^B (TS^2). A small rotation of the amino group allows the carbonyl group to pass through the *peri* area (TS^3). A second inversion of the amino group reduces the steric hindrance between the carbonyl oxygen atom and Me^B and restores the electrostatic attraction between donor and acceptor and the repulsion between the free electron pairs, leading to the ground state of the *P* enantiomer (GS^P). Whereas the carbonyl group rotates through the *peri* area, Me^A and Me^B of the amino group do not rotate or significantly change their positions. This mechanism of pseudo-rotation and inversion of the amino group explains the low Ar−C barriers. The similar barriers show that the carbonyl group, and not the bulky residue R, mainly rotates through the *peri* area.

A complete inversion of the NMe_2 group could again increase the steric hindrance at the carbonyl group. Therefore, a trigonal-planar transition state TS^5 is suggested: Merely changing the hybridization of the tetrahedral amino group would already begin to reduce the steric and electrostatic hindrance and additionally allow larger *peri* distances and thus result in low barriers of rotation (Figure 7c). This mechanism would mainly be influenced by substituents that destabilize the tetrahedral ground state and stabilize the trigonal-planar transition state.

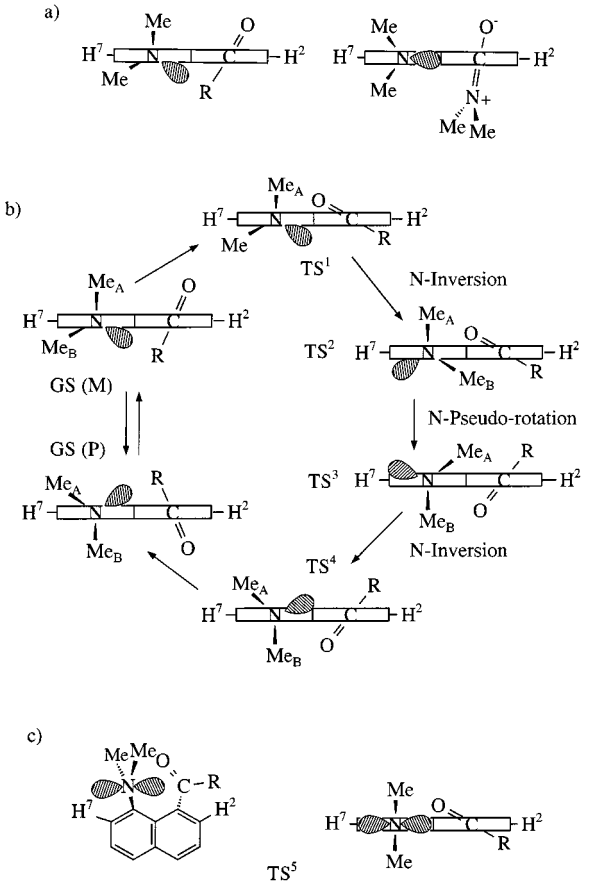


Figure 7. a) The ground state in amides is stabilized, the amide group is twisted out of the naphthalene plane by 112° and the lone pair of the nitrogen is directed towards the amide carbon atom; the electrostatic repulsion from the free electron pairs at the oxygen atom causes a destabilization of the tetrahedral amino group in ketones, the carbonyl group is twisted by 120°, and the lone pair of the nitrogen atom is directed toward the alkyl substituent;[18] b) interconversion of the enantiomers via pseudo-rotation and inversion of the tetrahedral amino group (see text); c) in a complete inversion, greater steric hindrance would partly compensate the weaker electrostatic repulsion; therefore, a trigonal-planar transition state (TS^5) is suggested; a planarization of the pyramidal NMe_2 group in the transition state to trigonal-planar would reduce the steric and electrostatic hindrance and additionally allow a larger *peri* distance

Both the pseudo-rotation−inversion and the proposed mechanism above avoid an energetically very costly transition state distortion of the naphthalene plane, which has been found for 1,8-(di-*tert*-butyl)naphthalenes. X-ray structure analyses[21] showed that the two benzene planes in 1,8-(di-*tert*-butyl)naphthalenes are significantly twisted by 43.4° in the ground state, which means that these molecules are chiral. Molecular mechanics calculations also implied a twisted naphthalene plane,[21] and dynamic NMR experiments[22] predicted a barrier of 26.4 kJ/mol for the rotation of the *tert*-butyl groups and a barrier of 92.2 kJ/mol for the enantiomerization. A barrier of rotation about the phenyl−naphthyl bond of 68.6 kJ/mol was determined for 1,8-diphenylnaphthalenes,[19] whereas 62.3 kJ/mol were measured for 1,4,5,8-tetraphenylnaphthalenes.[23] The decrease in the barrier (by 6.2 kJ/mol) caused by the higher substitution in the tetraphenylnaphthalenes indicates a twisting of the naphthalene plane in the transition state, which reduces the hindrance of the *peri*-substituted phenyl rings.

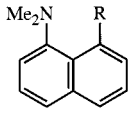
Fluorescence Properties and Anomalous Stokes Shifts

The difference between absorption and emission bands is called the Stokes shift. The *peri*-substituted compounds **1**−**9** showed large anomalous Stokes shifts (Table 1a). The largest Stokes shift was shown by the methyl ester **9**, with $\Delta\tilde{\nu}$ = 18354 cm^{-1}, whereas the ketones **1** and **2** had the smallest shifts. Increasing solvent polarity led to a further red shift of the emission bands. Table 2b and Table 2c show how the emission bands were shifted in three different solvents for compounds **1**, **8** and **9**. Obviously, a drastic increase of the dipole moment on excitation causes these shifts.

(Dimethylamino)naphthalene showed the greatest fluorescence intensity, introduction of the *peri*-CN substituent reduced the intensity by 50%, and introduction of acyl and amide groups decreased it even more (Table 2a). The relative fluorescence intensity also decreased with increasing solvent polarity (Figure 8, Table 2b). Only nitrile **8**, which served as a reference, showed good fluorescence quantum yields. It appeared that, going from *n*-hexane to toluene, the fluorescence became more intense; even in EtOH it was still about the same as in *n*-hexane (Table 2c). Only in MeCN did it appear to become significantly weaker (Table 2b). The ketones, however, showed very poor quantum yields, owing to the twisted carbonyl groups. The fluorescence lifetime of methyl ester **9** was small in *n*-hexane and EtOH, but much larger in 1,2,4-trimethylbenzene. There is fair agreement between the effect of the solvent on the fluorescence lifetime and on the fluorescence quantum yield.

In the case of the 1,8-DA-substituted naphthalenes the rotors are already twisted in the ground state. Therefore, the large Stokes shifts could be due to an emission from a so-called "TICT" state.[32] Such a process involves a charge transfer and a twisting of substituents, and an increase in polarity is expected to stabilize and favor the TICT state. In fact, Zinner[33] has observed a dual fluorescence of ester **9** at 77 K in EtOH: a large A-band at 548 nm and a much smaller B-band at 443 nm. This would be compatible with an emission from an equilibrium between a poorly populated LE state and a highly populated CT state. The smaller band at shorter wavelength would correspond to a more planar LE state and the larger band at longer wavelength to the twisted CT state. However, to explain the dual fluorescence at 77 K, it is necessary to consider not only the rotational isomerization around the Ar−N and Ar−C bonds, but also a change of the hybridization of the nitrogen atom from pyramidal to trigonal planar, as discussed before. More studies need to be performed on these unusually large Stokes shifts and the reported dual fluorescence of compound **9**.

Table 2. Selected fluorescence data for compounds **1**, **2**, and **4**–**9**



a) Anomalous Stokes shifts in increasing order; λ_{ex} = 300 nm, T = 25 °C, c = 1.0 × 10^{-4} mol/l, d = 1 cm

	R	Solvent	λ_{max}^{abs} (log ε) [nm]	λ_{max}^{em} [nm]	I_{rel}[a]	$\Delta\tilde{\nu}_{St}$ [cm^{-1}]
–	H	MeOH	–	417	1203	–
1	O=CMe	MeOH	300 (3.62)	404	2	8581
2	O=C–(*i*Pr)	MeOH	304 (3.67)	425	3	9365
8	CN	MeOH	340 (3.45)	514	655	9956
4	O=C–CH_2Ph	MeOH	298 (3.72)	455	17	11579
6	S=$CNMe_2$	CH_3CN	312 (3.83)	514	6	12596
5	O=C–(TriMP)[b]	MeOH	290 (4.12)	485	1	13864
7	O=$CNMe_2$	EtOH	295 (3.63)	545	12	15550
9	CO_2Me[c]	EtOH	290 (3.62)	620	–	18354

b) Solvent dependence of the anomalous Stokes shifts at 25 °C; ketone **1**: λ_{ex} = 300 nm, c = 1.0 × 10^{-4} mol/l, d = 1 cm; nitrile **8**: λ_{ex} = 340 nm, c = 1.05 × 10^{-5} mol/l, d = 1 cm.

	Solvent	λ^{abs} (log ε) [nm]	λ_{max}^{em} [nm]	I_{rel}[a]	$\Delta\tilde{\nu}_{St}$ [cm^{-1}]
1	*n*-Hexane	216 (5.0), 304 (4.0)	489	1650	12445
	$CHCl_3$	305 (3.7)	554	184	14736
	MeCN	216 (4.7), 303 (3.7)	566	51	15335
8	*n*-Hexane	216 (4.66), 258 (4.09), 345 (3.59)	454	411	6959
	$CHCl_3$	260 (4.12), 349 (3.46)	496	268	8492
	MeCN	218 (4.62), 257 (4.03), 340 (3.67)	512	95	9881

c) Corrected fluorescence data of nitrile **8** and ester **9**; λ_{ex} = 313 nm, T = 25 °C, d = 1 cm, c = 3 × 10^{-4} mol/l

	Solvent	λ_{max}^{abs} (log ε) [nm]	$^{em}_{max}$ [nm]	$\Delta\tilde{\nu}_{St}$ [cm^{-1}]	Q_F	τ_F [ns]
8	*n*-Hexane	345 (3.59)	461	7294	0.26	9.2
	EtOH	339 (3.67)	527	10523	0.23	12.8
	Toluene	348 (3.46)	489	8286	0.38	12.5
9	*n*-Hexane	295 (3.59)	500	13898	≤ 0.01	2.2
	EtOH	290 (3.62)	620	18354	<< 0.01	0.9
	1,2,4-TMB[d]	–	544	–	0.09	13.3

[a] Relative fluorescence intensity. – [b] TriMP: 3,4,5-trimethoxyphenyl. – [c] Corrected values. – [d] TMB: trimethylbenzene.

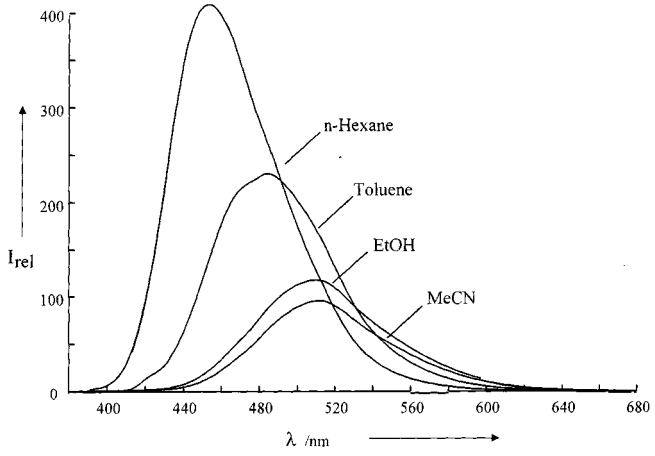


Figure 8. Anomalous Stokes shifts of nitrile **8**; increasing solvent polarity induced a red shift of the emission band and reduced the fluorescence intensity

Conclusion

Using ^{1}H NMR spectroscopy, barriers of rotation about Ar–N and Ar–C bonds have been determined and assigned for a series of *peri*-substituted naphthyl ketones. Strictly correlated rotations were found for the isopropyl, *tert*-butyl, and benzyl ketones, due to their tightly interlocked rotors. Less strongly correlated processes, in which the individual barriers could be distinguished, were found for the trimethoxyphenyl and the methyl ketone.

The surprisingly low barriers and similar Ar–C and Ar–N rotations – despite the differences in substituents – are due to the pseudo-rotation and inversion of the tetrahedral NMe_2 group. This process dramatically reduces the steric and electrostatic hindrance in the transition state, and also reduces an energetically costly twist of the naphthalene plane. As of the NMe_2 group a complete inversion would again increase the steric hindrance at the carbonyl group, a

trigonal-planar transition state is suggested, which additionally allows larger *peri* distances. The similar barriers indicate that, in the main pathway transition state, the carbonyl group passes the *peri* substituent.

The most impressive properties of these 1,8-DA-substituted compounds are the large anomalous Stokes shifts of up to 18354 cm^{-1}. These indicate that these compounds undergo a drastic increase in dipole moment upon excitation.

Experimental Section

Spectroscopy and Analysis: ^1H NMR spectra were recorded with a Bruker AW-80, WM-250, or ARX-400 instrument at 24 °C, with tetramethylsilane as internal standard. Temperatures were determined by samples of CH_3OH or 1,2-ethanediol.[24] Hexamethyldisilane or octamethylcyclotetrasiloxane served as internal standards for measurements at higher temperatures. The barriers were calculated using the coalescence method, in which the NMR shift difference $\Delta\nu_c$ is extrapolated to the coalescence temperature, using correction for the bandwidth of the signals and the equilibrium constant. For an uncoupled AB: $k_c = \frac{\pi}{\sqrt{2}}\Delta\nu_c$ with $\frac{b_E}{\Delta\nu_c}$ and K;[25] for a coupled AB: $k_c = \frac{\pi}{\sqrt{2}}\sqrt{\Delta\nu^2 + 6J^2}$ with $\frac{J_{AB}}{\Delta\nu_c}$ and .[26] The ^1H NMR spectrum of the naphthalene H atoms was simulated with the program LAME.[27] − IR spectra were measured with Beckman Acculab 1 or Jasco IR 810 spectrometers. − UV spectra were recorded with a Hitachi U-2000, luminescence spectra with a Hitachi F-3000 instrument. The latter were obtained for 10^{-4} M solutions, with a light path of 1 cm and are not corrected unless specified otherwise. − Melting points were determined with a Büchi SMP-20 or a SMP-530 apparatus and are corrected. − Column chromatography was carried out on ICN silica gel $60F_{254}$ (63−200 μm).

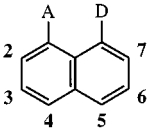
Synthesis: The naphthyl ketones **1**,[28] **2**−**5**,[29] and the thioamide **6**,[29] the amide **7**,[20] and ester **9**[20] were synthesized as reported earlier. 1-Cyano-8-(dimethylamino)naphthalene (**8**) was synthesized from 8-amino-1-bromonaphthalene (**11**).[18,30] Firstly, 8-amino-1-bromonaphthalene was methylated with dimethyl sulfate by a standard method;[31] then the cyano compound **8** was obtained using CuCN in a Rosenmund-von-Braun reaction.

1-Bromo-8-(dimethylamino)naphthalene (11): 8-Amino-1-bromonaphthalene (**10**)[30] (1.9 g, 8.55 mmol) was treated with dimethyl sulfate (2.7 mL, 28.3 mmol). Purification by column chromatography (*n*-hexane/diethyl ether, 5:1) resulted in a colorless (slightly yellow) liquid. Yield: 2.0 g (94%) of **11**. − ^1H NMR (250 MHz, $CDCl_3$, 24 °C, TMS): δ = 2.75 [s, 6 H, $N(CH_3)_2$], naphthalene H atom signals see Table 3.

1-Cyano-8-(dimethylamino)naphthalene (8): 1-Bromo-8-(dimethylamino)naphthalene (4.6 g, 18.4 mmol) and CuCN (1.93 g, 21.5 mmol, 15% excess) were heated under reflux in DMF (40 mL) for 4 h. Then the solvent was removed and the precipitate was dissolved in toluene. The mixture was added to a solution of $FeCl_3$ (7.36 g, 45.4 mmol), conc. HCl (1.84 mL), and water (11.1 mL), which was heated to 60−70 °C for 20 min to decompose the copper complex. The solution volume was adjusted to fit in a fluid-fluid extractor with H_2O/toluene. After 4 h of extraction, the solvent was evaporated and the product purified by column chromatography (petroleum ether/ethyl acetate, 5:1). Recrystallization from *n*-hexane resulted in bright yellow to bright green needles. Yield: 3.0 g (82%) of **8**. M.p. 75−76 °C. − ^1H NMR (250 MHz, $CDCl_3$, 24 °C, TMS): δ = 2.75 [s, 6 H, $N(CH_3)_2$], naphthalene H atom signals see Table 3. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (C_{ar}−H), 2990, 2920, 2860, 2830 (C_{ar}−H), 2780 (N−CH_3), 2200 (C≡N), 1600, 1560 (C=C_{ar}). − $C_{13}H_{12}N_2$ (196.25): calcd. C 79.56, H 6.16, N 14.27; found C 79.54, H 6.11, N 14.25.

Chromatography: The *peri*-substituted naphthyl ketones could not be separated or enriched on optically active sorbents [microcrystalline triacetylcellulose, tribenzoylcellulose, (+)-poly(tritylmethacrylate)/SiO_2, and tris(phenylcarbamoyl)cellulose/SiO_2], because the interconversion barriers were too low. Nor was separation of the enantiomers possible with the *tert*-butyl ketone **3**, which would have had a high enough barrier. The low k' values and the absent polarimetric detection shows that the interaction between the ketones and the optically active sorbent is very weak.

Table 3. ^1H NMR chemical shifts and coupling constants [Hz] of the aromatic H-atoms in *peri*-disubstituted naphthalenes in $CDCl_3$



	A	D	H^2	H^3	H^4	H^5	H^6	H^7
10	Br	NH_2	7.68 dd	7.13 m	7.62 dd	7.25 m	7.25 m	6.73 m
11	Br	NMe_2	7.75 dd	7.20 m	7.71 dd	7.47 dd	7.38 t	7.19 d
8	CN	NMe_2	7.96 dd	7.49 m	8.02 dd	7.62 dd	7.51 t	7.35 dd

	$^4J_{24}$	$^3J_{34}$	$^4J_{45}$	$^3J_{56}$	$^4J_{57}$	$^3J_{67}$
10	1.2	8.2	−	8.2	1.2	7.4
11	1.2	8.2	0.3	8.1	1.2	7.1
8	1.3	8.2	0.3	8.2	1.3	7.4

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