

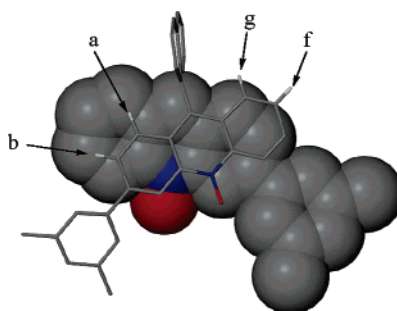
Highly Congested Nondistorted Diheteroarylnaphthalenes: Model Compounds for the Investigation of Intramolecular π -Stacking Interactions

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The rigid, highly congested structure of 1,8-diacridylnaphthalenes has been studied in solution and in the solid state. The unique geometry of these compounds forces the acridyl rings to undergo face-to-face interactions while rendering T-shaped orientations and face-to-edge interactions impossible. Crystallographic analysis shows that splaying between the heteroaryl rings decreases while twisting between the cofacial rings increases as the acridyl nitrogens of the 1,8-diacridylnaphthalene framework are subsequently oxidized. The *peri*-acridyl rings are slightly splayed but remain perfectly planar in all cases. The significant decrease in splaying indicates enhanced π - π attraction between the electron-rich acridyl *N*-oxide moieties, which is in agreement with recently reported symmetry-adapted perturbation theory calculations. The π -stacking and the molecular geometry between the acridyl rings observed in the solid state have been confirmed through in-solution studies showing characteristic proton NMR upfield shifts and optical properties indicative of static intramolecular arene-arene interactions. Acridyl protons located directly above the adjacent aryl moiety as a consequence of twisting between the heteroaryl rings were identified by COSY NMR measurements and found to intrude into the π -cloud and diamagnetic ring current of the neighboring acridine. Different shapes and strong red shifts of the fluorescence emission maxima of the diacridylnaphthalenes in comparison to parental acridyl monomers have been attributed to static excimer emission.

Introduction

It has been widely recognized that arene π -stacking plays a crucial role in biological systems, such as DNA and RNA,¹ molecular recognition,² and chemical engineering of new materials with intriguing properties including optical nonlinearity.³ Although π -stacking is a common motif in life and materials sciences,⁴ few ex-

amples that exclusively afford face-to-face interactions between aryl π -systems have been reported to date.⁵ The unique geometry of cyclophanes⁶ or pyridinophanes⁷ forces aromatic rings into a cofacial arrangement, which enables one to use this class of compounds as a model to study the nature of face-to-face and dipole-dipole interactions. The congested structure of [2.2]paracyclophanes

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and derivatives thereof impedes intramolecular face-to-edge interactions and thus provides a means to explicitly study π - π interactions albeit the aryl rings are highly distorted, which limits the use of these compounds.

Introduction of aryl¹⁸ or heteroaryl¹⁹ groups into the *peri* positions of naphthalene affords aromatic compounds providing an opportunity to study π -stacking and to develop new materials. Despite their exceptional stereochemical and electronic properties, very few applications of 1,8-diheteroarylnaphthalenes have been reported to date. Bahl et al. reported blue-transparent frequency-doubling devices based on 1,8-diheteroarylnaphthalenes with nonlinear optical properties.¹⁰ Watkinson et al. developed a 1,8-diarylnaphthalene-derived bis(manganese) complex exhibiting water splitting activity upon irradiation of visible light.¹¹ We have become interested in the stereodynamics of 1,8-diheteroarylnaphthalenes¹² and recently reported the use of 1,8-diacridylnaphthalenes for selective metal ion detection and enantioselective fluorosensing of chiral compounds.¹³ Herein, we

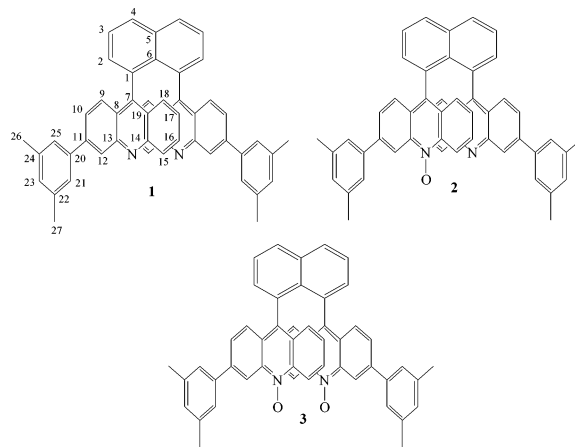


FIGURE 1. Structures of 1,8-diacridylnaphthalenes **1–3**. Because the molecules have an inversion center, the symmetry-related atoms are not labeled.

describe the crystallographic and spectroscopic investigation of the structure and intramolecular interactions of highly congested nondistorted 1,8-diacridylnaphthalenes exhibiting cofacial aryl groups that exclusively undergo face-to-face but not face-to-edge interactions in the solid state and in solution. The congested structure does not allow solvent molecules to enter the space between the *peri*-aryl rings and therefore excludes competition between π -stacking and solvation.

Results and Discussion

To elucidate the three-dimensional structure and intramolecular interactions of diacridylnaphthalenes, we decided to grow single crystals of diacridylnaphthalene **1**, diacridylnaphthalene *N*-oxide **2**, and diacridylnaphthalene *N,N'*-dioxide **3** for crystallographic analysis, Figure 1.

We were successful in preparing crystals suitable for X-ray analysis using isothermal evaporation and diffusion methods. Careful solvent evaporation of a solution of diacridine **1** in a 1:1 mixture of dichloromethane and acetonitrile afforded a monoclinic single crystal belonging to the *C*2/*c* space group, Table 1. Further crystallographic analysis revealed an eclipsed arrangement of the cofacial acridyl rings, which are slightly twisted, exhibiting a C7–C1–C1'–C7' torsion angle of 0.8°, Table 1.¹⁴ The acridyl moieties are splayed away from each other, forming an angle of 11.6°, Figure 2.¹⁵ As a result, the distance between C7 and C7' is 3.04 Å, whereas the distance between the two nitrogen atoms is increased to 4.38 Å.

Slow diffusion of diethyl ether into a dichloromethane solution of monoxide **2** gave a triclinic crystal belonging to the *P* $\bar{1}$ space group. Crystallographic analysis showed that **2** affords a twisted but less splayed solid-state structure than **1**, Figure 3. We determined the C7–C1–C1'–C7' torsion angle as 10.5°. Interestingly, oxidation of **1** decreases splaying of the acridyl moieties and results in a smaller splaying angle of only 8.3°. The distance

(14) Atoms C1, C6, and C1' are in one plane in all three single-crystal structures. We therefore use the angle between the two acridylnaphthyl bonds (C1–C7 and C1'–C7') and the naphthalene plane to describe the torsion (C7–C1–C1'–C7') between the acridyl rings.

(15) The splaying angle of **1–3** is defined as the angle between the extrapolated acridyl planes.

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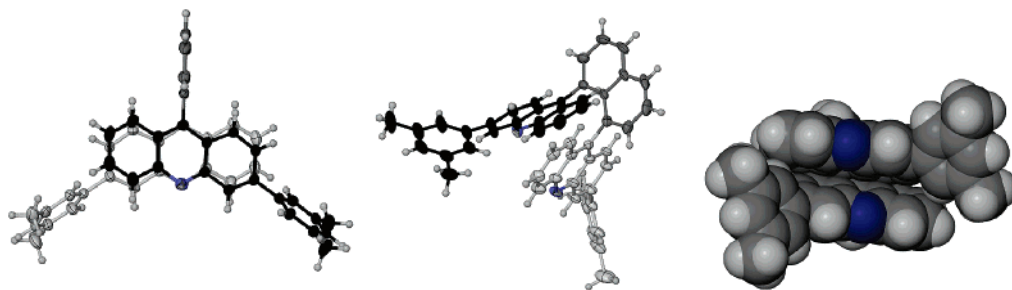


FIGURE 2. Front and side view (left) and space-filling model (right) of the single-crystal structure of *anti*-diacridine **1**. The front 3,5-dimethylphenylacridyl ring is shown in dark for better clarity.

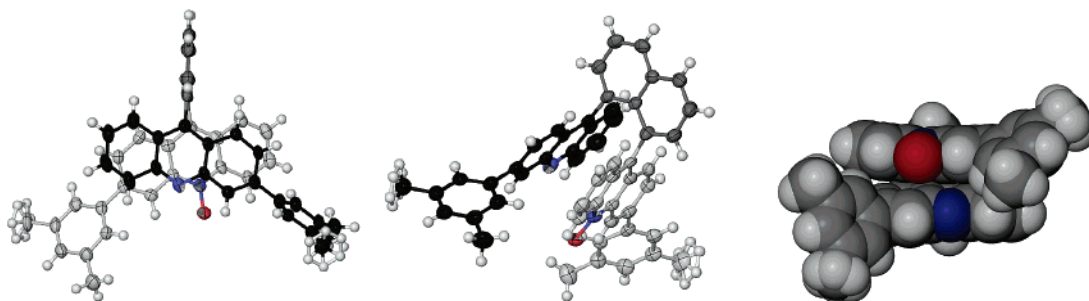


FIGURE 3. Front and side view (left) and space-filling model (right) of the solid-state structure of diacridyl naphthalene *N*-oxide **2**. One 3,5-dimethylphenylacridyl ring is shown in dark for better clarity.

TABLE 1. Selected Data for Single Crystals of **1**, **2**, and **3**

	1	2	3 ·CH ₂ Cl ₂
empirical formula	C ₅₂ H ₃₈ N ₂	C ₅₂ H ₃₈ N ₂ O	C ₂₇ H ₂₁ Cl ₂ NO
fw	690.84	706.84	446.35
temp (K)	173(2)	183(2)	173(2)
cryst syst	monoclinic	triclinic	monoclinic
space group	<i>C2/c</i>	<i>P1</i>	<i>P2/n</i>
unit cell dimensions	<i>a</i> = 16.1895(13) Å <i>b</i> = 10.3998(9) Å <i>c</i> = 21.2941(18) Å α = 90° β = 92.680(2)° γ = 90°	<i>a</i> = 10.8531(14) Å <i>b</i> = 12.2879(16) Å <i>c</i> = 14.4533(19) Å α = 108.655(3)° β = 90.794(3)° γ = 91.440(3)°	<i>a</i> = 13.8017(12) Å <i>b</i> = 11.3080(10) Å <i>c</i> = 15.0290(14) Å α = 90° β = 113.116(2)° γ = 90°
vol (Å ³)	3581.3(5)	1825.2(4)	2157.2(3)
Z	4	2	4
cryst size (mm ³)	0.30 × 0.20 × 0.10	0.50 × 0.40 × 0.30	0.50 × 0.50 × 0.20
distance C7–C7' (Å)	3.04	2.95	2.93
distance N–N (Å)	4.38	3.77	3.85
torsion C7–C1–C1'–C7' (deg)	0.8	10.5	23.8
Splaying (deg)	11.6	8.3	5.3
intermolecular hydrogen bonding (Å)	2.60 (N–H4)	2.88 (N–H4) 2.96 (N–H4') 2.93 (O–H4)	2.55 (O–H4) 2.23 (O–CH ₂ Cl ₂)
intramolecular hydrogen bonding (Å)			3.20 (O–H21')

between C7 and C7' was determined as 2.95 Å and is similar to that observed in the single crystal of **1**. However, the distance between the two nitrogen atoms is only 3.77 Å, which can be attributed to reduced repulsion and attractive π – π -stacking between the slightly parallel-displaced acridyl rings.

Oxidation of monoxide **2** provides *N,N*-dioxide **3** exhibiting two electron-rich acridyl *N*-oxide rings. A cocrystal of dioxide **3** and one molecule of dichloromethane was prepared by isothermal evaporation of dichloromethane, Table 1. The single crystal obtained with **3** is monoclinic and belongs to the *P2/n* space group. We found that the acridyl rings are twisted about 23.8° but remain almost perfectly cofacial. The splaying angle

of **3** was determined as only 5.3°, Figure 4. The separation between the acridyl atoms C7 and C7' is 2.93 Å. Although the rings are barely splayed, the distance between the two nitrogen atoms was found to be 3.85 Å, which can be attributed to the parallel-displaced geometry, Table 1. The acridyl rings are therefore much closer than in **1** and **2** despite the expected increase in electronic repulsion between the electron-rich aryl π -systems. This behavior is in contrast to the Hunter–Sanders model that qualitatively predicts substituent effects on π – π -interactions on the basis of predominant electrostatic interactions between independently treated negatively charged π -clouds and positively charged aryl σ -frameworks.¹⁶ Accordingly, conversion of the relatively electron-deficient

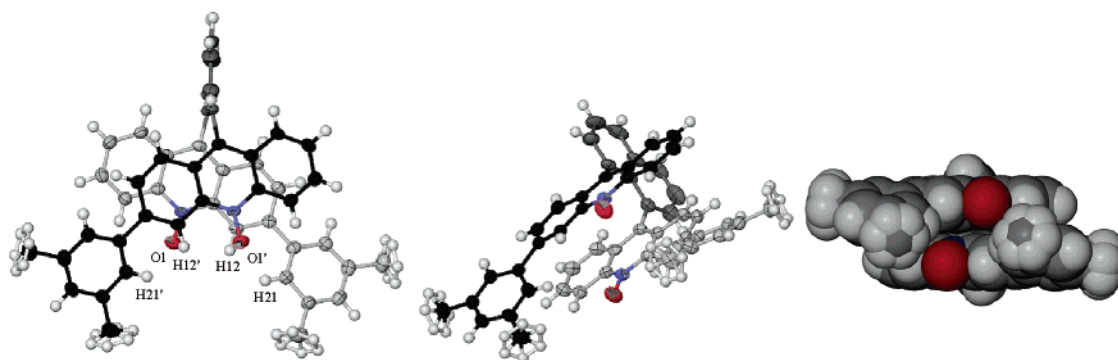


FIGURE 4. Front and side view (left) and space-filling model (right) of the single-crystal structure of diacridylnaphthalene *N,N'*-dioxide **3**. The front 3,5-dimethylphenylacridyl ring is shown in dark for better clarity.

1,8-diacridylnaphthalene **1** to the π -electron-rich *N,N'*-dioxide **3** should result in increased π - π -electrostatic repulsion. However, ab initio calculations based on the symmetry-adapted perturbation theory recently reported by Sinnokrot and Sherrill show that solely considering electrostatics while neglecting dispersion, induction, and exchange repulsion is insufficient to accurately predict substituent effects on π - π -stacking. They found that the incorporation of electron-donating groups into arenes should indeed increase face-to-face interactions.^{5e,17} The decrease in splaying accompanying subsequent oxidation of 1,8-diacridylnaphthalene **1** to monoxide **2** and dioxide **3** can therefore be attributed to different degrees of repulsion, whereas the increasing torsion between the acridyl *N*-oxide rings is expected to reduce dipole-dipole repulsion.

The crystal lattices of **1–3** are stabilized by intermolecular hydrogen bonding between the aryl heteroatoms and the hydrogens of the naphthyl ring of the adjacent molecule in addition to face-to-face and face-to-edge interactions, Figure 5. The intermolecular N–H4 hydrogen bond length in the crystal of **1** was determined as 2.60 Å. Monoxides **2** have two N–H4 (2.88 and 2.96 Å) hydrogen bonds and one O–H4 (2.93 Å) hydrogen bond. The oxygen atoms of dioxide **3** participate in strong hydrogen bonding to the hydrogens in position 4 of the naphthyl group of the adjacent molecule (2.55 Å) and also to one hydrogen of cocrystallized dichloromethane (2.23 Å). There is also crystallographic evidence for weak intramolecular hydrogen bonding within *N,N'*-dioxide **3**. The *N*-oxide functionalities undergo hydrogen bonding to the aryl CH groups of the 3,5-dimethylphenyl moieties of the opposite arene system, Figure 4. The corresponding O1–H21' and O1'–H21 distances were determined as 3.20 Å. Notably, similar N–O \cdots H bonding interactions of pyridine *N*-oxides have been observed in solution and in the solid state.¹⁸ We therefore assume that, in addition to π - π -interactions and packing forces, intramolecular

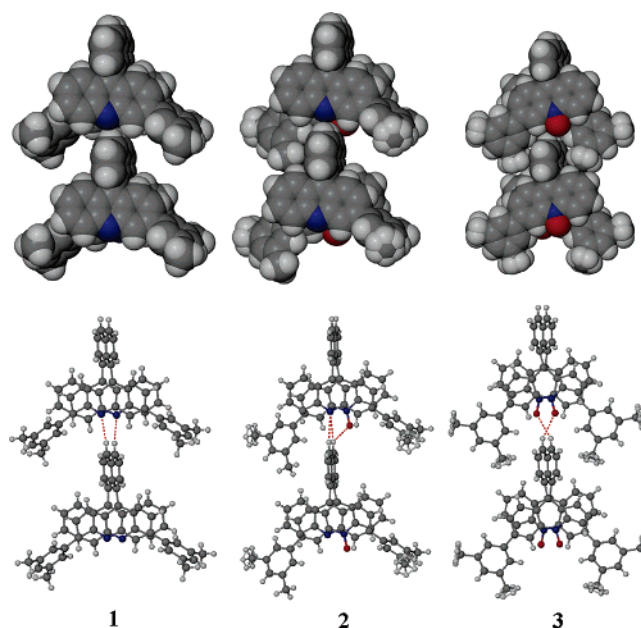


FIGURE 5. Space-filling (top) and ball-and-stick (bottom) models illustrating intermolecular hydrogen bonding between diacridylnaphthalenes **1–3**.

hydrogen bonding stabilizes the condensed structure of **3** in the solid state.

Transannular π - π -interactions including face-to-face interactions between parallel arenes and face-to-edge interactions or homoconjugation in rigid T-shaped geometries have been observed in cyclophanes, spiropolyenes, and dihydropyrenes and are usually accompanied by high-field shifts in the ¹H NMR spectrum.¹⁹ To compare the solid-state structures of diacridylnaphthalenes with the favored or time-averaged structure in solution, we decided to assign all protons of **1** and **3** and of the corresponding monomers 3-(3,5-dimethylphenyl)-9-bromoacridine (**4**) and 3-(3,5-dimethylphenyl)-9-bromoacridine *N*-oxide (**5**) by COSY NMR experiments. For the congested diheteroarylnaphthalenes **1** and **3** we expected that, as a consequence of the twisting between the heteroaryl rings, which is most evident in the crystal structure of **3**, certain protons would be located directly above the opposite acridyl moiety and intrude into its

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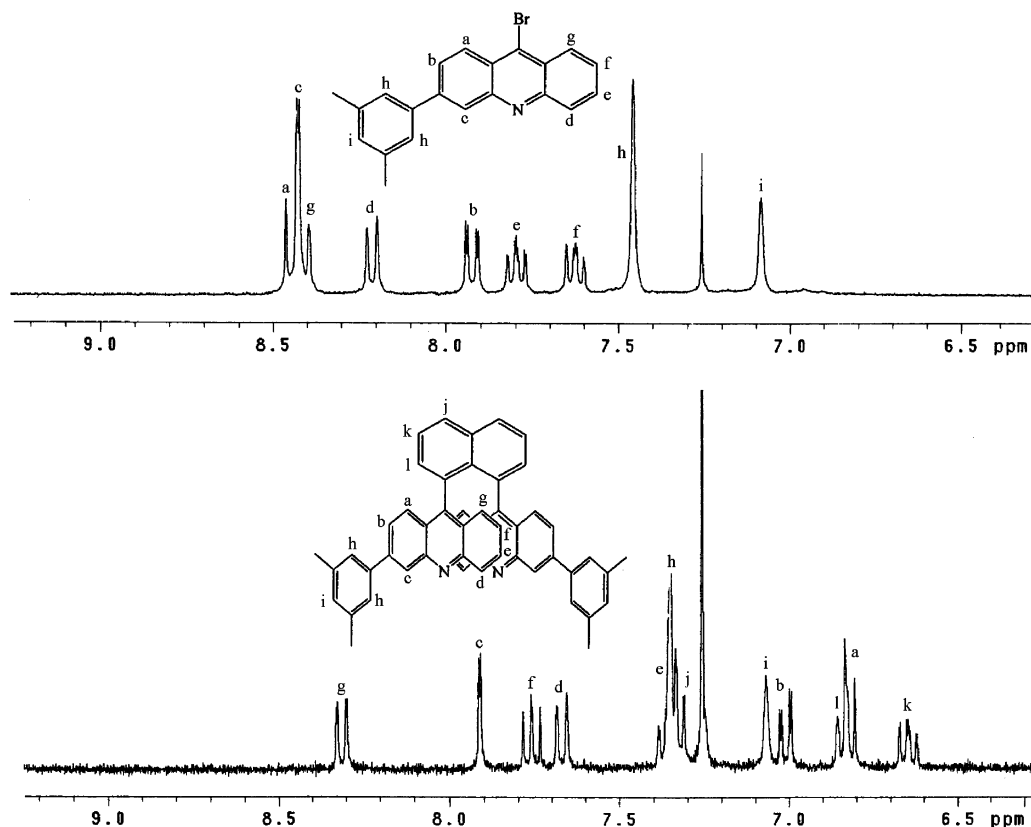


FIGURE 6. ^1H NMR assignments of diacridylnaphthalene **1** and 9-bromo-3-(3,5-dimethylphenyl)acridine (**4**) in CDCl_3 based on COSY experiments.

π -cloud and diamagnetic ring current. These protons would experience significant shielding and thus a pronounced upfield shift compared to the corresponding proton signals of the monomeric bromide derivatives, Figures 6 and 7. Comparison of the ^1H NMR spectrum of **1** and **4** or **3** and **5**, respectively, shows that most signals experience an upfield shift because of anisotropic shielding in the diacridylnaphthalene framework. In particular, protons a and b are significantly shielded in diacridylnaphthalene **1**, exhibiting an upfield shift of 1.60 and 0.97 ppm. Comparison of the NMR spectrum of **3** and **5** reveals that protons a and b are similarly upfield shifted by 1.63 and 0.87 ppm. By contrast protons f and g seem to have similar chemical environments in the monomers and diacridylnaphthalenes and remain almost at the same chemical shift.

Since protons a and b appear to be significantly upfield shifted through intramolecular π -stacking while protons f and g are almost unaffected, we assume that the same parallel-displaced geometry between the acridyl moieties observed with N,N' -dioxide **3** in the solid state is favored in solution. Accordingly, twisting of both acridyl moieties toward each other reduces the size of the cleft of diacridylnaphthalenes **1–3** and places protons a and b into the anisotropic ring current of the adjacent acridyl group, whereas protons f and g are located at the periphery of the π -cloud of the neighboring ring and therefore afford chemical shifts similar to those of the protons in the corresponding monomeric acridines **4** and **5**, Figure 8.

The rigid architecture and the close proximity of the two acridyl rings in diacridylnaphthalenes **1** and **3** should also result in quite different optical properties compared

to the parent bromoacridines **4** and **5**, Figures 9 and 10. The UV spectrum of **1** does not vary significantly from that of monomeric acridine **4** above 280 nm, whereas **3** shows a red shift of the high-wavelength absorptions in comparison to bromoacridine **5**, indicating enhanced π - π -interactions between the associated acridyl N -oxide chromophores as was observed in the solid state. A comparison of the fluorescence maxima of diacridines **1** and **3** and the corresponding monomers shows that the former undergo a strong red shift that can be attributed to excimer emission of the proximal acridyl rings. The two fluorescence maxima of **4** in acetonitrile were determined to be 420 and 435 nm, whereas **1** has one maximum at 560 nm. Similarly, the emission maxima of **5** were observed at 490 and 520 nm, while diacridine **3** shows one maximum at 570 nm. Interestingly, crystallographic analysis of 1,8-diquinolynaphthalenes reveals similarly congested structures in the solid state. However, we have found that these compounds are nonrigid in solution and do not show any red shift and excimer fluorescence in the UV and fluorescence spectra.^{12d} In contrast to 1,8-diacridylnaphthalenes **1–3**, diquinolynaphthalenes and all other 1,8-diarylnaphthalenes reported to date undergo rotation about the (hetero)aryl-naphthalene bond in solution and are likely to afford T-shaped geometries and CH/π -interactions with solvents that diffuse into the space between the fluxional aryl rings that are only cofacial in the solid state. The concurrent solid- and solution-state observations of nondistorted 1,8-diacridylnaphthalenes **1–3** are in agreement with NMR, X-ray, and ab initio measurements of 5,6-diarylacenaphthenes reported by Whiting and co-workers and a consequence

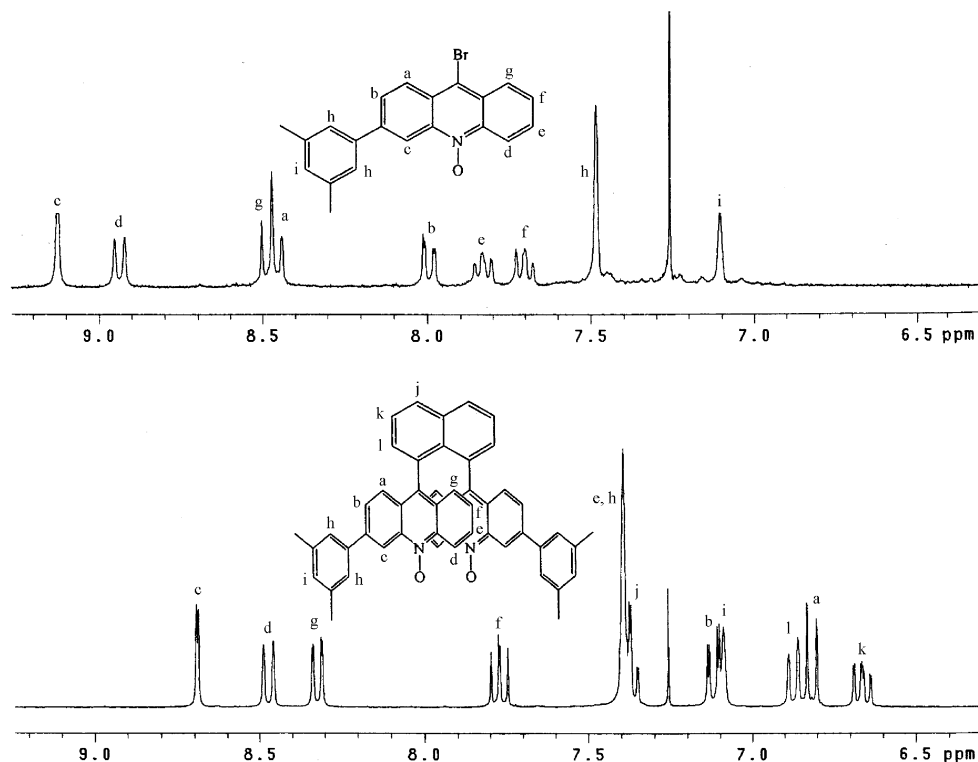


FIGURE 7. ^1H NMR assignments of diacridylnaphthalene N,N' -dioxide **3** and 9-bromo-3-(3,5-dimethylphenyl)acridine N -oxide (**5**) in CDCl_3 based on COSY experiments.

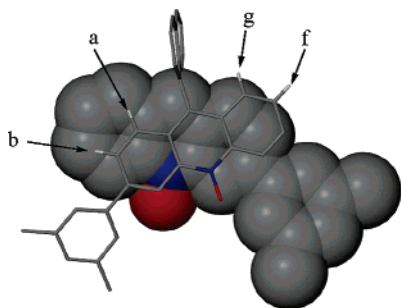


FIGURE 8. Illustration of the torsional structure of diacridylnaphthalenes and the location of protons a, b, f, and g using the single-crystal structure of N,N' -dioxide **3**. The space-filling view of the acridyl moiety in the rear represents its π -cloud to demonstrate the effect of π -stacking and torsion on the ^1H NMR shifts.

of the unique geometry of these molecules as they render face-to-edge interactions and solvation between the cofacial arene rings impossible.²⁰

Conclusions

The study of close contacts of cofacial aryl rings is fundamental to crystal engineering and biological chemistry, for example, to obtain a better understanding of DNA base pair stacking. Experimental studies of face-to-face interactions are often impeded by competing face-to-edge interactions or arene distortions inherent to rigid cyclophanes. The incorporation of two acridyl rings into

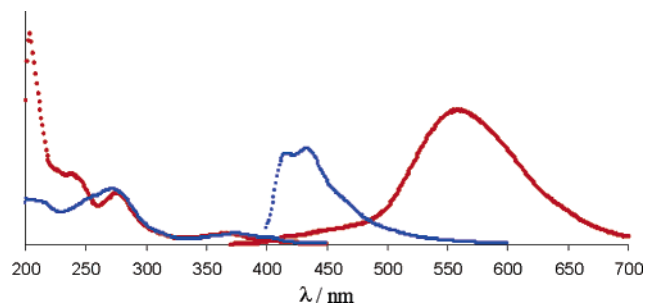


FIGURE 9. UV and fluorescence spectrum of **1** (red line) and **4** (blue line). The concentration was 3.5×10^{-5} M in acetonitrile. The excitation wavelength was 360 nm.

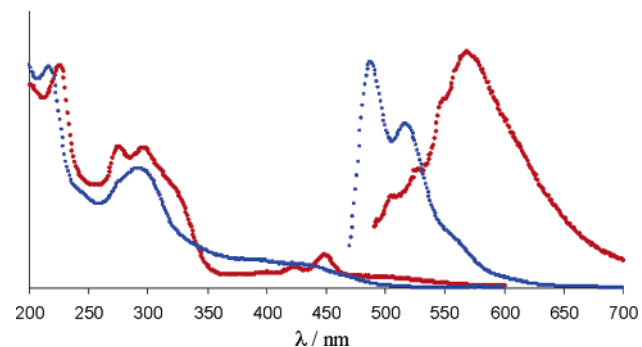


FIGURE 10. UV and fluorescence spectrum of **3** (red line) and **5** (blue line). The concentration was 3.5×10^{-5} M in acetonitrile. The excitation wavelength was 470 nm.

the *peri* positions of naphthalene generates highly congested 1,8-diacridylnaphthalenes **1–3** exhibiting a well-defined geometry that excludes solvation between the cofacial arenes and T-shaped orientations leading to face-

(20) Cross, W.; Hawkes, G. E.; Kroemer, R. T.; Liedl, K. R.; Loerting, T.; Nasser, R.; Pritchard, R. G.; Steele, M.; Watkinson, M.; Whiting, A. *J. Chem. Soc., Perkin Trans.* **2001**, 459–467.

to-edge interactions and thus allows systematic studies of intramolecular face-to-face interactions in the solid state and in solution. The association of cofacial nondistorted acridyl moieties has been verified by single-crystal structure analysis of **1–3** in conjunction with NMR studies and UV and fluorescence spectroscopy. Transannular π - π -interactions have been found to increase with consecutive oxidation of 1,8-diacridylnaphthalene **1** to its N,N' -dioxide **3**, which is in agreement with ab initio calculations recently reported by Sherrill showing that incorporation of electron-donating substituents increases π - π -interactions between arenes.

Experimental Section

Monoxide **2** was formed through deoxygenation during crystallization efforts of **3**. NMR spectra were obtained at 300 MHz (^1H NMR) and 75 MHz (^{13}C NMR) using CDCl_3 as the solvent. Chemical shifts are reported in parts per million relative to the resonance for TMS. UV absorption and fluorescence spectra were collected under nitrogen using 3.5×10^{-5} M solutions of compounds **1**, **3**, **4**, and **5** in degassed acetonitrile. Acridines **1** and **4** were excited at 360 nm, and acridine N -oxides **3** and **5** were excited at 470 nm.

9-Bromo-3-(3,5-dimethylphenyl)acridine N -Oxide (5**).** To a solution of 9-bromo-3-(3',5'-dimethylphenyl)acridine (0.05 g, 0.14 mmol) in 3 mL of methylene chloride was added

dropwise chloroperbenzoic acid (0.063 g, 0.28 mmol) in 2 mL of methylene chloride. The reaction mixture was stirred at room temperature for 5 h and concentrated in vacuo. Purification of the orange residue by flash chromatography (50:1 methylene chloride/ethyl acetate) afforded **5** (0.48 g, 91%) as a yellow solid: ^1H NMR δ = 2.44 (s, 6H), 7.11 (s, 1H), 7.49 (s, 2H), 7.62–7.73 (m, 1H), 7.80–7.85 (m, 1H), 8.00 (dd, J = 1.65 Hz, J = 9.07 Hz, 1H), 8.44–8.51 (m, 2H), 8.94 (dd, J = 1.1 Hz, J = 9.07 Hz, 1H), 9.13 (s, 1H); ^{13}C NMR δ = 21.6, 117.0, 120.1, 120.4, 125.7, 126.3, 126.8, 128.4, 128.6, 128.7, 128.8, 130.8, 131.4, 138.9, 139.0, 140.3, 140.4, 144.2. Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{BrNO}$: C, 66.68; H, 4.26; N, 3.70. Found: C, 66.88; H, 4.28; N, 3.99.

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Supporting Information Available: Synthetic procedures for **1**, **3**, and **4**, X-ray crystallographic data of **1**, **2**, and **3**, and COSY NMR spectra of **1**, **3**, **4**, and **5** (CIF, PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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