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Bent Structure and Dynamic Stereochemistry of Chiral Acridinium Cations

Benoît Laleu,[†] Christelle Herse,[†] Bo W. Laursen,[§] Gérald Bernardinelli,[‡] and Jérôme Lacour*,[†]

Département de Chimie Organique, Université de Genève, quai Ernest-Ansermet 30, CH-1211 Genève 4, Switzerland, Nano-Science center, Department of Chemistry, Universitatesparken 5, DK-2100 Copenhagen, Denmark, and Laboratoire de Cristallographie, Université de Genève, quai Ernest-Ansermet 24, CH-1211 Genève 4, Switzerland

jerome.lacour@chiorg.unige.ch

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Chiral acridinium cations, easily prepared by reaction of enantiopure primary amines and tris-(2,6-dimethoxy)trityl cation, display restricted rotations around the C(sp^3)−N(sp^2) bond. A bending of the aromatic backbone and "out-of-plane" displacements of C(9) and N(10) atoms are enforced if bulky amines are introduced.

Twisted aromatics, such as helicenes, corannulenes, homoazulenes, and substituted fluoranthenes, have been studied for their interesting geometries and chemical and physical properties.[1] *N*-Alkyl acridinium cations (Figure 1), electron acceptors in photophysical and bioorganic studies,[2] have often been structurally characterized and shown to possess, to the contrary of the previous molecules, an essentially planar aromatic skeleton with "in-plane" substituents at the 9 and 10 positions.[3]

Herein, we show that the introduction of bulky substituents at the nitrogen atom of the acridinium ring leads to (i) a restricted rotation around the C(sp^3)−N(sp^2) bond, (ii) a bending of the aromatic backbone (γ angle, Table 2), and (iii) "out-of-plane" displacements of atoms 9 and 10 (α, β, $\Delta N(10)$, and $\Delta C(9)$, Table 2) as observed by NMR spectroscopy or X-ray diffraction analyses. Previously, examples of dynamic conformational isomerism have been reported for structurally related 9-anthryl derivatives.[4,5] There have also been reports of barriers to rotation about carbon−nitrogen bonds in hindered pyridinium systems,[6] and relationships between structure, molecular energy, and geometry have been calculated for alkyl-substituted *N*-methylpyridinium cations.[7] However, to our knowledge, dynamic stereochemistry and physical evidence of structural deformations enforced by the presence of sterically hindered substituents have not been described for acridinium compounds.

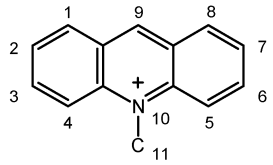

FIGURE 1. General structure of *N*-alkyl acridinium compounds.

Results and Discussion

Recently, the reactions of primary amines with the tetrafluoroborate salt (**1**) of the known tris(2,6-dimethoxyphenyl)carbenium ion were reported (Scheme 1).[8] *n*-Propylamine, benzylamine, or aniline were shown to react with **1** and form the corresponding 9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-10-*n*-acridinium salts (**2a**−**c**, respectively). These compounds are the result of two

[†] Département de Chimie Organique.
[§] Nano-Science center.
[‡] Laboratoire de Cristallographie.

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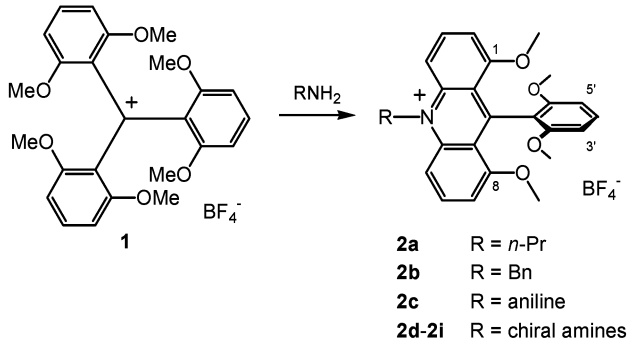
SCHEME 1. Synthesis of 9-(2,6-Dimethoxyphenyl)-1,8-dimethoxy-10-*n*-acridinium Salts 2a−i



consecutive *ortho* S_NAr reactions of the primary amines; further reaction leads to the synthesis of interesting [4]helicenium cations.[9] The mild conditions for the preparation of these acridinium moieties and the rapidity of their formation led us to imagine the possible reaction of bulkier amines, and chiral derivatives in particular. Enantiopure compounds **d**−**i** (Figure 2) were tested and reactions at room temperature yielded the corresponding acridinium tetrafluoroborate salts **2d**−**i** in good yields (85−93%) and chemical purities. Several other chiral amines were tested, including 1,2,3,4-tetrahydro-naphthalen-1-ylamine, 1-naphthalen-1-yl-ethylamine, indan-1-ylamine, and 1-(4-methoxy-phenyl)-ethylamine; decomposition of the corresponding acridinium adducts into acridine **3** occurred during the synthesis or at room temperature once isolated (Figure 3).[10]

Room temperature ^{1}H NMR analysis of the new salts, **2d**−**i**, revealed rather different results depending upon the nature of the chiral amines. Whereas broad resonances were observed for the protons of **2d**, **2e**, and **2f**, sharp individual and separated signals were displayed for all acridinium protons and (1,8)-methoxy substituents in compounds **2g**, **2h**, and **2i** (see the Supporting Information and Figure 4); in the latter cases, an NMR differentiation was also noticed for the 2′,6′-methoxy groups and 3′,5′-hydrogen atoms of the phenyl moiety attached at carbon 9. These observations were indicative of a restricted rotation around the N(sp^2)−C(sp^3) bond,[6] and prompted us to study the stereodynamic process in more detail.

Variable-temperature (VT) NMR experiments on salts **2d**−**i** were thus performed. Compounds **2g**, **2h**, and **2i** were dissolved in DMSO-d_6 and analyzed by ^{1}H NMR spectroscopy at elevated temperatures (≤150 °C). A dynamic conformational isomerism was detected for **2h** and **2i** as coalescences of analogous NMR signals occurred (Table 1 and Supporting Information). The separated methoxy groups were particularly easy to monitor (e.g. **2h**, Figure 4).[11] Rotation barriers were determined by line-shape analysis (WinDNMR) of the broadened exchange signals that gave the rate constants (k). A representative experimental and calculated line shape is depicted in Figure 4. The barriers were determined at

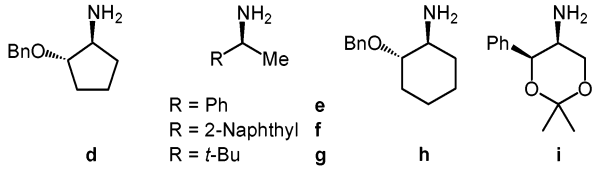


FIGURE 2. Chiral primary amines used in the formation of acridinium cations **2d**−**i**.

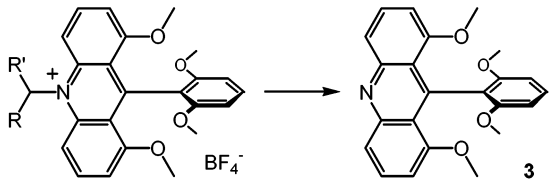


FIGURE 3. Thermal decomposition of some acridinium salts into **3**.

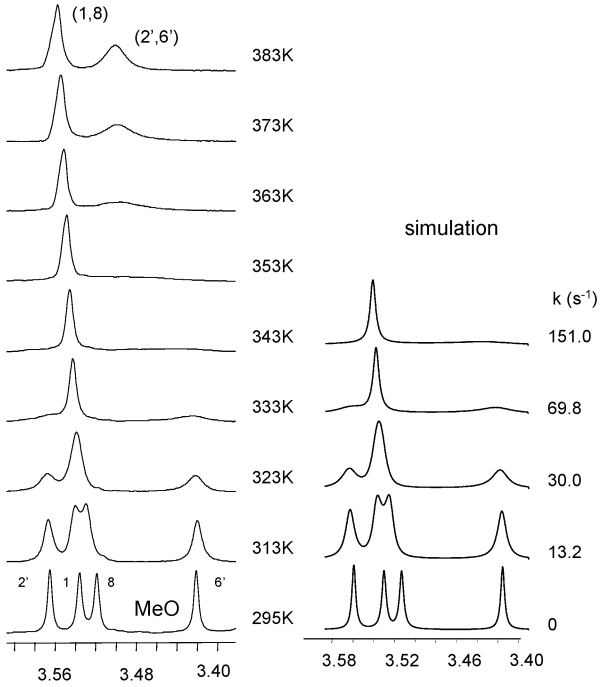


FIGURE 4. Experimental (DMSO-d_6, 400 MHz, 295−383 K) and best-fit calculated ^{1}H NMR spectra of **2h** (MeO region, δ 3.59−3.39 ppm).

different temperatures and the activation parameters ($\Delta H^‡$, $\Delta S^‡$, $\Delta G^‡$) were calculated by using the Arrhenius and Eyring equations (see the Supporting Information), the activation entropy ($\Delta S^‡$) being normally small for an intramolecular rotational process (Table 1). For **2g**, no broadening of any signals could be observed upon heating the sample up to 100 °C ($\Delta G^‡$ > 83.7 kJ·mol^{-1}).[12] However, a decomposition of **2g** into acridine **3** was noticed at temperatures higher or equal to 90 °C (Figure 3).[13]

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(10) Dealkylation at high temperature of pyridinium salts was observed by Balaban and Katritzky. See ref 6d and references therein.

(11) For line-shape analysis, the system was analyzed as a four-site coalescence of four singlets into two singlets.

(12) The relationship $\Delta G^‡ = RT_c(22.96 + \ln(T_c/\Delta\nu))$ was used to determine the activation energy, $\Delta G^‡$, from the coalescence temperature, T_c (K), and the frequency separation of the peaks, $\Delta\nu$ (Hz).

(13) When heated in DMSO-d_6, compounds **2e** and **2f** decompose into acridine **3** at 60 and 80 °C, respectively. No such behavior was observed for **2d** ($T \leq 150$ °C).

TABLE 1. Relevant Data for the Stereodynamics among Acridinium Salts 2d−i

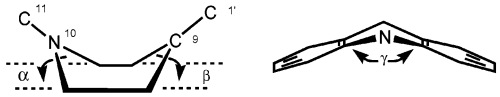
entry	acridinium	$\Delta\delta^a$	$\Delta G^{\ddagger\,b}$	$\Delta H^{\ddagger\,b}$	$\Delta S^{\ddagger\,c}$
1[d]	**2d**	0.000[e]	49.8	50.4	2.1
2[d]	**2e**	0.083[e]	51.4	51.8	1.1
3[d]	**2f**	0.148[e]	52.6	52.7	0.5
4[f]	**2g**	0.276[e]	>83.7	[g]	[g]
5[d]	**2h**	0.144[e]	70.3	70.5	0.6
6[d]	**2i**	0.084[e]	75.8	76.9	3.8

[a] In ppm. [b] In kJ·mol^{-1}. [c] In J·mol^{-1}·K^{-1}. [d] Activation parameters calculated by using line-shape analysis (WinDNMR) and $\Delta G^{\ddagger}$ reported for a 25 °C temperature. [e] (2′,6′)-MeO. [f] $\Delta G^{\ddagger}$ estimated by using the relationship $\Delta G^{\ddagger} = RT_c(22.96 + \ln(T_c/\Delta\nu))$; $T_c > 373$ K; $\Delta\nu = 6.6$ Hz. [g] Not applicable.

TABLE 2. Deformation Parameters of the Central Pyridinium Rings of 2a,[8b] 2b,[8b] 2d, and 2g from Crystallographic Results

entry	acridinium	α^a	β^a	γ^b	$\Delta N(10)^c$	$\Delta C(9)^c$
1	**2a**	8.1	6.9	171.5	0.09	0.09
2	**2b**[d]	1.7	2.7	178.4	−0.02	0.05
3	**2b**[d]	8.1	12.1	173.3	0.09	0.05
4	**2d**	11.7	4.1	171.0	0.14	0.05
5	**2g**[d]	18.2	14.7	160.9	0.22	0.19
6	**2g**[d]	18.1	10.5	163.5	0.22	0.13

[a] α and β (deg) are the dihedral angle of the envelope at N(10) and C(9), respectively. [b] γ (deg) is the bent angle corresponding to the folding of the central ring along the N(10)···C(9) line. [c] $\Delta N(10)$ and $\Delta C(9)$ (Å) are the out-of-plane displacements of the N10 and C9 atoms. [d] The asymmetric unit contains two independent acridinium molecules.



For compounds **2d**, **2e**, and **2f**, low-temperature NMR experiments were necessary to determine the barriers of rotation as the reduced steric hindrance of amines **d**−**f** induced faster stereodynamics. The compounds were dissolved in $CDCl_3$ and analyzed by VT-NMR. At 223 K, most aromatic and methoxy protons were separated (Supporting Information). Rotation barriers were determined by line-shape analysis and are reported in Table 1.

The series of $\Delta G^{\ddagger}$ values in Table 1 revealed a rather strong influence of the nature of the stereogenic moieties on the rotation barrier.[14] Ring size is particularly important as the "replacement" of a cyclopentyl (**2d**) by a cyclohexyl (**2h**) framework increases the $\Delta G^{\ddagger}$ by ∼20.5 kJ·mol^{-1} (Table 1, entries 1 and 5). Not surprisingly, the higher barrier of energy is detected for compound **2g** derived from 1,2,2-trimethyl-propylamine. As for the pyridinium systems,[6] all facts indicate that the N^+−C bond, being shorter than a classical C−C bond, leads to rather high rotation barriers.

Careful analysis of the crystal structures of **2a** and **2b** indicated the possibility of structural deformations of the acridinium ring,[8b] as a bending of the aromatic skeleton ($\gamma = 171.5-178.4°$) and "out-of-plane" displacements for atoms N(10) and C(9) ($\alpha = 1.7-8.1°$, $\beta = 2.7-12.1°$) were erratically noticed (Table 2, entries 1−3). It was then

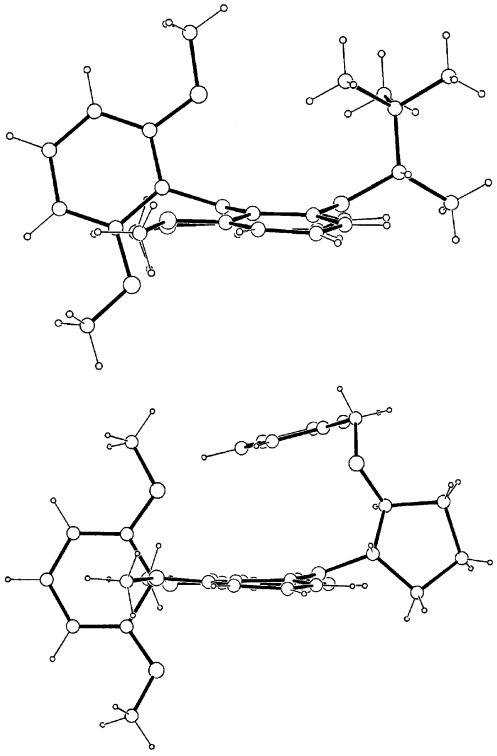


FIGURE 5. Lateral views of **2g** (top) and **2d** (bottom).

debatable whether the sterically hindered substituents linked at N(10) would also influence the geometry of the acridinium moiety by promoting, for instance, definite deformations of the aromatic backbone.

X-ray quality crystals of **2g** were obtained by slow diffusion of Et_2O to a CH_2Cl_2 solution and measured at low temperature (180 K, Figure 5). Rather large deviations from planarity were observed for the aromatic ring ($\alpha = 18.1-18.2°$, $\beta = 10.5-14.5°$, $\gamma = 160.9-163.5°$, Table 2, entries 5 and 6). The N(10)−C(11) bond length in **2g** is 1.52 Å, slightly longer than that in **2a** and **2b** (1.50 Å). Crystals of **2d** were obtained under similar conditions (Et_2O/CH_2Cl_2), and X-ray structural analysis (200 K, Figure 5) revealed a more "in-plane" position for the dimethoxyphenyl appendage ($\beta = 4.1°$), while the 2-benzyloxy-cyclopentyl moiety was bent "out-of-plane" ($\alpha = 11.7°$). The N(10)−C(11) bond length is 1.51 Å. Overall, the structure of **2d** seems to be "intermediate" between **2a** and **2b**, and the more deformed **2g**.[15] In the preferred solid-state conformations of **2d** and **2g**, the C(11)−H bonds are almost parallel to the "plane" of the acridinium ring (see the Supporting Information).[5,16] This is in contrast with the structures of **2a** and **2b** in which the *n*-propyl and benzyl side chains are perpendicular,[5] the remaining methylene protons being orientated at (±)-30° to the "plane".

The presence of bulky centers in proximity to N(10) seems therefore to enforce the natural trend for deforma-

(14) To the exception of compounds **2e** and **2f** for which, as could be expected, similar energy values were found, 1-phenyl and 2-naphthyl having similar steric influence.

(15) Contrary to **2g** for which no stacking interaction was observed, all aromatic moieties of **2d** are involved in weak stacking interactions which, to our point of view, do not affect the deformation of the central pyridinium ring.

(16) In the pyridinium systems, a preferred conformation was proposed in which the hydrogen atom of the stereogenic sp^3 carbon is in the plane of the pyridine ring. See ref 6.

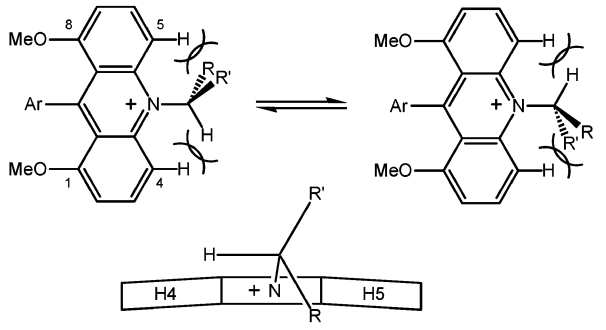


FIGURE 6. Strain induced by the secondary alkyl groups and consecutive deformation, R being smaller than R′. H···H4 = 1.76 and 1.87 Å for **2d** and **2g**, respectively.

tion observed in **2a** and **2b**. In view of the results obtained by NMR spectroscopy, it is logical to consider that the presence of the sterically hindered substituents induces a strain in the acridinium framework (Figure 6) that can only be compensated for by a deformation of aromatic skeleton and an elongation of the $N^+(sp^2)-C(sp^3)$ bond.[7,17]

In conclusion, we have shown that the linkage of sterically hindered substituents to the nitrogen atom of an acridinium moiety provokes a restricted rotation around the N(10)−C(11) bond and, in the case of strong steric hindrance, both a bend of the aromatic backbone and "out-of-plane" displacements of atoms 9 and 10 are observed.

Experimental Section

General Procedure for the Synthesis of 2d−h. To a solution of compound **1** (300 mg, 0.59 mmol) in 1-methyl-2-pyrrolidone (NMP, 6.0 mL) was added 2.5 equiv of chiral enantiopure amine (**d**−**h**, 1.47 mmol). The initial purple reaction mixture immediately turned red. After 20 h at room temperature, the crude was poured into aqueous HBF_4 (13.0 mL, 50%) and water was added (2.0 mL). The resulting red precipitate was collected by filtration and washed with water (2 × 2.0 mL) and Et_2O (4 × 3.0 mL) to afford the desired tetrafluoroborate salts as red solids; no further purification was necessary.

(*S*,*S*)-9-(2,6-Dimethoxy-phenyl)-1,8-dimethoxy-10-(2-*trans*-benzyloxy-cylopentyl)-9,10-dihydro-acridinium tetrafluoroborate (2d) was synthesized following the general procedure with (*S*,*S*)-2-*trans*-benzyloxy-cylopentylamine (302 mg, 1.47 mmol) to give (*S*,*S*)-**2d** (333 mg, 0.51 mmol, 87%): $[\alpha]^{20}_D$ −295 (6.44×10^{-3}, CH_2Cl_2);[18] mp 227 °C; UV/vis (CH_2Cl_2, λ_{max} (log ϵ)) 513 (3.82), 411 (3.92), 358 (3.64), 291 (4.87), 248 (4.27), 227 (4.41); IR 3005, 2985, 2950, 2842, 1599, 1579, 1501, 1473, 1435, 1343, 1252, 1103, 1065, 1029, 972, 816, 771, 744, 696 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.14 (t, ^3J = 8.3 Hz, 2H), 7.930 (s, br, 2H), 7.45 (t, ^3J = 8.3 Hz, 1H), 7.17 (d, ^3J = 8.3 Hz, 2H), 7.08 (m, 1H), 7.00 (t, ^3J = 7.6 Hz, ^3J = 7.1 Hz, 2H), 6.82 (d, ^3J = 8.3 Hz, 2H), 6.69 (d, ^3J = 7.1 Hz, 2H), 5.07 (m, 1H), 4.89 (m, 1H), 4.20 (d, ^2J = 12.6 Hz, 1H), 4.13 (d, ^2J = 12.6 Hz, 1H), 3.54 (s, 6H), 3.53 (s, 6H), 2.75 (m, 1H), 2.57 (m, 1H), 2.47 (m, 1H), 2.23 (m, 1H), 2.12 (m, 1H), 1.91 (m, 1H); ^{13}C NMR (DMSO-d_6 100 MHz) δ 160.0 (C), 157.0 (C), 155.2 (C), 139.3 (CH), 137.5 (C), 129.4 (CH), 127.9 (CH), 127.5 (CH), 127.0 (CH), 119.9 (C), 118.9 (C), 110.5 (CH), 106.9 (CH), 103.7 (CH), 80.0 (CH), 72.9 (CH), 70.1 (CH_2), 57.2 (CH_3), 55.8 (CH_3), 30.2 (CH_2), 28.1 (CH_2), 21.4 (CH_2); MS *m*/*z* (ES) 550.4 (M^+, 34%), 466.3 (24%), 376.2 (100%).

(*S*)-9-(2,6-Dimethoxy-phenyl)-1,8-dimethoxy-10-(1-phenyl-ethyl)-9,10-dihydro-acridinium tetrafluoroborate (2e) was synthesized following the general procedure with (*S*)-1-phenyl-ethylamine (178 mg, 1.47 mmol) to give (*S*)-**2e** (304 mg, 0.54 mmol, 91%): $[\alpha]^{20}_D$ −50 (5.77×10^{-3}, CH_2Cl_2);[18] mp 162 °C; UV/vis (CH_2Cl_2, λ_{max} (log ϵ)) 512 (3.79), 413 (3.91), 358 (3.68), 290 (4.88), 248 (4.32), 227 (4.47); IR 3019, 2978, 2945, 2840, 1595, 1575, 1497, 1474, 1458, 1434, 1338, 1273, 1251, 1144, 1044, 1032, 816, 762, 704 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.10 (s, br, 2H), 7.98−7.75 (s, br, 2H), 7.44 (t, ^3J = 8.3 Hz, 1H), 7.41 (d, ^3J = 7.8 Hz, 2H), 7.36 (m, 2H), 7.16 (d, ^3J = 7.8 Hz, 3H), 6.81 (d, ^3J = 8.6 Hz, 2H), 3.57 (s, 6H), 3.53 (s, 6H), 2,29 (d, ^3J = 7.1 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 160.1 (C), 157.6 (C), 155.3 (C), 139.6 (CH, br), 139.0 (C), 129.5 (CH), 129.3 (CH), 127.8 (CH), 125.3 (CH), 120.1 (C), 118.9 (C), 116.5 (C, br), 110.7 (CH, b), 106.8 (CH), 103.7 (CH), 63.0 (CH), 57.1 (CH_3), 56.0 (CH_3), 17.8 (CH_3); MS *m*/*z* (ES) 480.4 (M^+, 28%), 376.2 (100%).

(*S*)-9-(2,6-Dimethoxyphenyl)-1,8-dimethoxy-10-(1-naphthalen-2-yl-ethyl)-9,10-dihydro-acridinium tetrafluoroborate (2f) was synthesized following the general procedure with (*S*)-1-naphthalen-2-yl-ethylamine (252 mg, 1.47 mmol) to give (*S*)-**2f** (309 mg, 0.50 mmol, 85%): $[\alpha]^{20}_D$ −160 (6.56×10^{-3}, CH_2Cl_2);[18] mp 153 °C; UV/vis (CH_2Cl_2, λ_{max} (log ϵ)) 512 (3.83), 413 (3.91), 358 (3.60), 291 (4.87), 229 (5.05); IR 3011, 2984, 2948, 2835, 1616, 1596, 1574, 1496, 1476, 1461, 1435, 1336, 1274, 1253, 1230, 1091, 1050, 986, 818, 766, 758, 701 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.25−7.82 (s, br, 4H), 8.03 (s, 1H), 7.97 (m, 1H), 7.90 (m, 2H), 7.56 (m, 2H), 7.51 (q, ^3J = 6.8 Hz, 1H), 7.45 (t, ^3J = 8.3 Hz, 1H), 7.16 (s, br, 2H), 6.96 (dd, ^3J = 8.6 Hz, ^4J = 1.5 Hz, 1H), 6.83 (d, ^3J = 8.3 Hz, 2H), 3.59 (s, 6H), 3.54 (s, 6H), 2.41 (d, ^3J = 6.8 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 160.1 (C), 157.7 (C), 155.3 (C), 139.5 (CH, b), 136.6 (C), 132.9 (C), 132.1 (C), 129.5 (CH), 129.0 (CH), 128.1 (CH), 127.6 (CH), 126.9 (CH), 126.7 (CH), 124.3 (CH), 123.2 (CH), 120.2 (C), 118.9 (C), 110.5 (CH, br), 106.9 (CH), 103.7 (CH), 63.5 (CH), 57.1 (CH_3), 56.0 (CH_3), 17.9 (CH_3); MS *m*/*z* (ES) 530.3 (M^+, 40%), 466.3 (30%), 179.4 (100%).

(*S*)-9-(2,6-Dimethoxy-phenyl)-1,8-dimethoxy-10-(1,2,2-trimethyl-propyl)-9,10-dihydro-acridinium tetrafluoroborate (2g) was synthesized following the general procedure with (*S*)-1,2,2-trimethyl-propylamine (149 mg, 1.47 mmol) to give (*S*)-**2g** (290 mg, 0.53 mmol, 90%): $[\alpha]^{20}_D$ +330 (5.45×10^{-3}, CH_2Cl_2);[18] mp 174 °C; UV/vis (CH_2Cl_2, λ_{max} (log ϵ)) 516 (3.76), 415 (3.91), 292 (4.87), 227 (4.41); IR 3010, 2989, 2941, 2841, 1604, 1579, 1498, 1473, 1433, 1340, 1251, 1098, 1060, 1023, 964, 846, 767, 733, 701 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.32 (d, ^3J = 9.6 Hz, 1H), 8.18 (m, 2H), 8.11 (t, ^3J = 8.1 Hz, ^3J = 9.1 Hz, 1H), 7.41 (t, ^3J = 8.3 Hz, 1H), 7.19 (d, ^3J = 3.0 Hz, 1H), 7.17 (d, ^3J = 3.0 Hz, 1H), 6.83 (d, ^3J = 8.3 Hz, 1H), 6.73 (d, ^3J = 8.3 Hz, 1H), 5.89 (q, ^3J = 7.3 Hz, 1H), 3.65 (s, 3H), 3.54 (s, 3H), 3.52 (s, 3H), 3.38 (s, 3H), 2.24 (d, ^3J = 7.3 Hz, 3H), 0.77 (s, 9H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 159.3 (C), 156.7 (C), 156.4 (C), 154.2 (C), 145.1 (C), 141.9 (C), 139.3 (CH), 137.5 (CH), 129.4 (CH), 120.4 (C), 120.3 (C), 118.9 (C), 112.9 (CH), 111.1 (CH), 107.0 (CH), 106.6 (CH), 104.1 (CH), 103.1 (CH), 71.5 (CH), 57.0 (CH_3), 56.9 (CH_3), 55.9 (CH_3), 55.8 (CH_3), 28.1 (CH_3), 16.8 (CH_3); MS *m*/*z* (ES) 460.4 (M^+, 30%), 376.2 (100%).

(*S*,*S*)-9-(2,6-Dimethoxy-phenyl)-1,8-dimethoxy-10-(2-*trans*-benzyloxy-cylohexyl)-9,10-dihydro-acridinium tetrafluoroborate (2h) was synthesized following the general procedure with (*S*,*S*)-2-*trans*-benzyloxy-cylopentylamine (281 mg, 1.47 mmol) to give (*S*,*S*)-**2h** (349 mg, 5.47 mmol, 93%): $[\alpha]^{20}_D$ −120 (6.56×10^{-3}, CH_2Cl_2);[18] mp 187 °C; UV/vis (CH_2Cl_2, λ_{max} (log ϵ)) 511 (3.80), 409 (3.91), 291 (4.86), 249 (4.28), 227 (4.38); IR 3010, 2989, 2941, 2841, 1738, 1598, 1575, 1501, 1473, 1432, 1338, 1275, 1254, 1203, 1108, 1052, 1029, 846, 767, 733, 701 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz)

(17) It is likely that bulky nonstereogenic amines (cyclohexylamine, 9*H*-fluoren-9-ylamine) will induce similar deformations.

(18) Cations **2d**−**i** are effective dyes absorbing light efficiently in most of the visible region (ref 8). Very dilute solutions and restricted wavelengths were required to measure the specific optical rotations.

δ 8.23 (d, ^3J = 9.4 Hz, 1H), 8.18 (t, ^3J = 9.4 Hz, 1H), 8.11 (d, ^3J = 9.1 Hz, 1H), 7.90 (t, ^3J = 8.1 Hz, ^3J = 8.8 Hz, 1H), 7.44 (t, ^3J = 8.3 Hz, 1H), 7.19 (d, ^3J = 7.6 Hz, 1H), 7.08 (d, ^3J = 8.1 Hz, 1H), 7.06 (d, ^3J = 7.3 Hz, 1H), 6.92 (t, ^3J = 7.6 Hz, ^3J = 7.3 Hz, 2H), 6.83 (t, ^3J = 8.3 Hz, ^3J = 8.1 Hz, 2H), 6.47 (d, ^3J = 8.3 Hz, ^3J = 7.1 Hz, 2H), 5.53 (m, 1H), 4.63 (m, 1H), 4.18 (d, ^2J = 12.4 Hz, 1H), 3.95 (d, ^2J = 12.4 Hz, 1H), 3.57 (s, 3H), 3.54 (s, 3H), 3.52 (s, 3H), 3.42 (s, 3H), 2.81 (m, 1H), 2.50 (m, 2H), 1.87 (m, 3H), 1.67 (m, 1H), 1.47 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 160.1 (C), 159.7 (C), 156.6 (C), 155.7 (C), 154.9 (C), 143.9 (C), 140.8 (C), 139.8 (CH), 138.2 (CH), 137.2 (C), 129.2 (CH), 127.8 (CH), 127.3 (CH), 127.2 (CH), 119.9 (C), 119.6 (C), 119.0 (C), 110.0 (CH), 110.2 (CH), 106.7 (CH), 103.7 (CH), 103.5 (CH), 74.1 (CH), 71.3 (CH), 68.4 (CH_2), 57.2 (CH_3), 57.0 (CH_3), 55.8 (CH_3), 55.8 (CH_3), 31.2 (CH_2), 29.3 (CH_2), 24.6 (CH_2), 22.8 (CH_2); MS *m*/*z* (ES) 564.4 (M^+, 100%), 466.3 (16%), 376.2 (14%), 179.4 (50%).

(*S*,*S*)-9-(2,6-Dimethoxyphenyl)-1,8-dimethoxy-10-(2,2-dimethyl-4-phenyl[1,3]dioxan-5-yl)-9,10-dihydro-acridinium Tetrafluoroborate (2i). To a solution of compound **1** (300 mg, 0.59 mmol) in NMP (6.0 mL) was added (*S*,*S*)-2,2-dimethyl-4-phenyl[1,3]dioxan-5-ylamine **i** (305 mg, 1.47 mmol). The initial purple reaction mixture immediately turned red. After 20 h at room temperature, NMP was distilled under reduced pressure (81 °C, 10 mmHg). Then Et_2O (30 mL) was added to the residual red oil. The red precipitate was collected by filtration and washed with Et_2O (3.0 mL) to afford the titled compound (334 mg, 0.51 mmol, 87%). No further purification was necessary: $[\alpha]^{20}_D$ +140 (6.53×10^{-3}, CH_2Cl_2);[18] mp 128 °C; UV/vis (CH_2Cl_2, λ_{max} (log ϵ)) 521 (3.73), 415 (3.88), 293 (4.77), 248 (4.32), 228 (4.48); IR 3010, 2989, 2941, 2841, 1600, 1575, 1501, 1473, 1432, 1386, 1338, 1254, 1108, 1052, 1029, 964, 846, 767, 733, 701 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.07 (d, ^3J = 9.1 Hz, 1H), 8.25 (m, 1H), 8.18 (m, 2H), 7.36 (t, ^3J = 8.3 Hz, 1H), 7.15 (d, ^3J = 7.8 Hz, 1H), 7.05 (d, ^3J = 7.8 Hz, 1H), 6.92−6.82 (m, 5H), 6.80−6.73 (m,1H), 6.73 (d, ^3J = 8.3 Hz, 1H), 6.70 (d, ^3J = 8.3 Hz, 1H), 6.09 (d, ^3J = 7.1 Hz, 1H), 4.82 (dd, ^2J = 13.1 Hz, ^3J = 7.6 Hz, 1H), 4.69 (dd, ^2J = 13.1 Hz, ^3J = 5.6 Hz, 1H), 3.49 (s, 3H), 3.46 (s, 3H), 3.41 (s, 3H), 3.40 (s, 3H), 1.80 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 159.8 (C), 159.4 (C), 156.5 (C), 155.4 (C), 154.8 (C), 143.8 (C), 141.6 (C), 139.7 (CH), 137.9 (CH), 135.1 (C), 129.1 (CH), 127.2 (CH), 127.0 (CH), 124.7 (CH), 119.3 (C), 119.2 (C), 119.0 (C), 113.8 (CH), 110.0 (CH), 106.7 (CH), 106.6 (CH), 103.9 (CH), 103.3 (CH), 100.9 (CH), 70.3 (CH), 61.3 (CH), 59.7 (CH_2), 57.0 (CH_3), 56.9 (CH_3), 55.8 (CH_3), 55.7 (CH_3), 27.0 (CH_3), 21.0 (CH_3); MS *m*/*z* (ES) 566.3 (M^+, 65%), 376.2 (100%).

9-(2,6-Dimethoxy-phenyl)-1,8-dimethoxy-acridine (3). **3** was usually isolated by recrystallization (MeOH) from crude reaction mixtures: mp 275 °C; UV/vis (CH_2Cl_2, λ_{max} (log ϵ)) 489 (4.47), 390 (4.63), 281 (5.52), 273 (5.51), 244 (5.22), 228 (5.24); IR 3296, 3178, 3090, 2960, 2850, 1642, 1620, 1587, 1519, 1472, 1267, 1256, 1098, 965, 818, 759, 721 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.13 (t, ^3J = 8.3 Hz, 2H), 7.81 (d, ^3J = 8.6 Hz, 2H), 7.43 (t, ^3J = 8.3 Hz, 1H), 7.11 (d, ^3J = 7.8 Hz, 2H), 6.79 (d, ^3J = 8.3 Hz, 2H), 3.53 (s, 6H), 3.52 (s, 6H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 158.5 (C), 155.6 (C), 140.9 (C), 137.7 (CH), 129.2 (CH), 118.8 (C), 118.7 (C), 112.2 (CH), 106.3 (CH), 103.6 (CH), 56.7 (CH_3), 55.8 (CH_3); MS *m*/*z* (EI) 375 (M^+, 100%), 283 (15%); HRMS calcd for $C_{23}H_{21}NO_4$ (M^+) 375.1471, found 375.1469.

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Supporting Information Available: VT-NMR and lineshape analyses of all new compounds (**2d**−**i**), collective spectral data (^{1}H NMR), and CIF files of **2d** and **2g** (CCDC 207160 and CCDC 207159). This material is available free of charge via the Internet at http://pubs.acs.org.

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