

Regioselective Photodimerization of 9-Substituted Acridizinium Salts in the Solid State

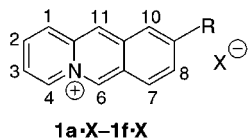
Heiko Ihmels,^{*,†} Dirk Leusser,[‡] Matthias Pfeiffer,[‡] and Dietmar Stalke^{*,‡}

University of Würzburg, Institutes of Organic Chemistry and Inorganic Chemistry, Am Hubland, D-97074 Würzburg, Germany

Received March 15, 1999

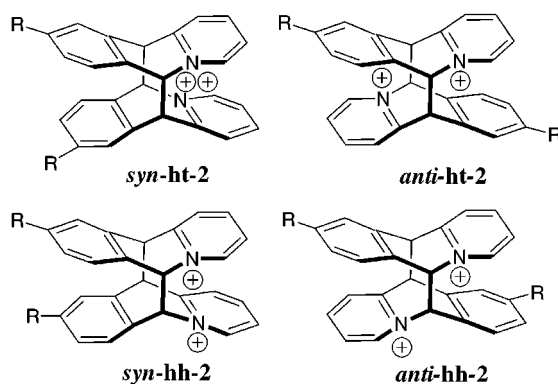
Introduction

Solid-state organic photoreactions have attracted much attention, since there is a growing number of remarkably selective transformations upon irradiation in the crystalline medium.¹ Among the reactions that have been investigated in the solid state, the photoinduced [4+4] cycloaddition is of special interest due to its high potential in organic synthesis.² Acridizinium salt derivatives,³ which dimerize on irradiation in a remarkably clean reaction, are ideal compounds for such studies. However, except for the investigation of the influence of the counterion on the solid-state dimerization of the parent compound **1a** and 9-methylacridizinium salt (**1b**), no systematic investigations of the solid-state photochemistry of this class of compounds are known.^{4,5}



- 1a**: R = H; X = Br, ClO₄
1b: R = Me
1c: R = Cl; X = Br or BF₄
1d: R = Br; X = Br or ClO₄
1e: R = OMe; X = ClO₄
1f: R = NH₂; X = Br or ClO₄

Single crystals of the parent compound **1a** were reported to undergo a topochemical photodimerization in the solid state to give exclusively the *anti*-head-to-tail dimer **anti-ht-2a**,⁴ but it was also shown that irradiation of the acridizinium salt **1a** in the polycrystalline state yields all four possible regioisomers **2**.⁵ For synthetic applications, however, the requirement of single crystals for a selective transformation is rather inconvenient, since single-crystal growth is often tedious and time-consuming work. Thus, for a selective arrangement of the



a: R = H; b: R = Me; c: R = Cl; d: R = Br; e: R = OMe; f: R = NH₂

chromophores in the polycrystalline state, it may be necessary to introduce additional intermolecular attractive or repulsive interactions to align the photoactive system properly.

Herein, we report the strategy to control the regioselectivity of the [4+4] photocycloaddition of the acridizinium chromophore in the solid state, namely the attachment of a π -donor substituent at the 9-position of these compounds. In addition to the repulsion between the quarternary nitrogen atoms, the orientation of two acridizinium molecules toward each other in the solid state should be governed by the attractive electronic interactions between the π -donor substituents and the quarternary nitrogen atoms to acquire an ideal *anti*-head-to-tail preorganization for a selective solid-state photodimerization. Although, such donor–acceptor interactions have been frequently used in crystal engineering for the selective photodimerization of some alkenes in the crystalline state⁶ and for selective solid-state cross-cycloadditions of mixed two-component crystals,^{1d} there are no examples to control the regioselectivity of [4+4] photocyclodimerization in the solid state by this method. Consequently, the solid-state photochemistry of the four 9-substituted acridizinium salts **1c–f** was investigated as a systematic application of this concept.

Results and Discussion

The amino-substituted acridizinium salt **1f** has been already reported to give exclusively the head-to-tail dimers on photolysis in solution.⁷ Irradiation of the 9-substituted acridizinium salts **1c–e** in acetonitrile or methanol solution resulted in all four regioisomers **2c–e**, as was determined by ¹H NMR spectroscopy. The formation of the photodimers **2** was indicated by the appearance of the characteristic NMR signals of the bridgehead protons. In all cases, the mixture of the photoproducts could not be separated by the usual chromatographic methods and the determination of the product ratio by ¹H NMR spectroscopy was impossible due to substantial overlap of the proton signals. In the case of derivative **1c**, small proportions of other unidentified byproducts were observed in the ¹H NMR spectrum

* E-mail: ihmels@chemie.uni-wuerzburg.de. Phone: +49-931-888 5337. Fax: +49-931-888 4606.

[†] Institute of Organic Chemistry.

[‡] Institute of Inorganic Chemistry.

(1) For reviews, see: (a) *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH Publishers: New York, 1991. (b) *Reactivity in Molecular Crystals*; Ohashi, Y., Ed.; VCH Publishers: New York, 1994. (c) Sakamoto, M. *Chem. Eur. J.* **1997**, *3*, 684. (d) Ito, Y. *Synthesis* **1998**, 1. (e) Ihmels, H.; Scheffer, J. R. *Tetrahedron* **1999**, *55*, 885.

(2) (a) Sieburth, S.; Cunard, N. T. *Tetrahedron* **1996**, *52*, 6251. (b) Kaupp, G. *Angew. Chem.* **1992**, *104*, 435; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 422.

(3) Bradsher, C. K. In *Comprehensive Heterocyclic Chemistry*; Boulter, A. J., McKillop, A., Eds.; Pergamon Press: Oxford, U.K., 1985; Vol. 2, p 525.

(4) (a) Wang, W. N.; Jones, W. *Tetrahedron* **1987**, *43*, 1273. (b) Wang, W. N.; Jones, W. *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 227. (c) Kearsley, D. K. In *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987; p 69.

(5) Lehnberger, C.; Scheller, D.; Wolff, T. *Heterocycles* **1997**, *10*, 2033.

(6) (a) Kaupp, G.; Frey, H.; Behmann, G. *Chem. Ber.* **1988**, *121*, 2135. (b) Vansant, J.; Toppet, S.; Smets, G.; Declercq, J. P.; Germain, G.; Van Meersche, M. *J. Org. Chem.* **1980**, *45*, 1565.

(7) Ihmels, H. *Tetrahedron Lett.* **1998**, *39*, 8641.

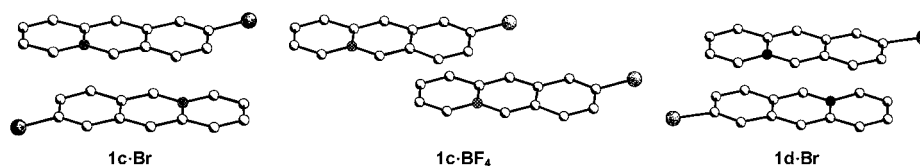


Figure 1. Arrangement of acridizinium salts **1c·Br**, **1d·Br**, and **1c·BF₄** in the solid state. A pair of the two closest molecules is shown, and hydrogen atoms and counteranions are omitted for clarity.

(multiplets at δ 4.0, 4.8, 6.1) besides the dimers **2c**; however, it was shown by ¹H NMR spectroscopy that these byproducts disappeared without the formation of new products when the crude reaction mixture was allowed to stand at room temperature for 1 day. Thus, we assume that the unknown products revert to the salt **1c**.

Solid-state irradiation of acridizinium salts **1c·Br**, **1d·Br**, and **1e·ClO₄** afforded the *anti*-head-to-tail dimers exclusively, which was indicated by only one set of signals in the ¹H NMR spectrum. Full conversion of **1c·Br** and **1d·Br** was achieved after 2 days, and in 1 week for **1e·ClO₄**. In the case of the acridizinium salt **1d·Br**, recrystallization from MeOH, MeOH/ethyl acetate, MeOH/2-propanol, or MeOH/acetone, followed by irradiation of the solid sample, led exclusively to the dimer *anti*-**ht-2d** in each case even when the solid sample did not have single-crystal quality. The acridizinium salts **1c·BF₄** (crystallized from water or methanol/toluene), **1d·ClO₄** (water or acetonitrile), **1f·Br** (methanol or methanol/ethyl acetate), and **1f·ClO₄** (water) were photoinert in the solid state.

The structural assignment of the isolated dimers *anti*-**ht-2** was made by comparison with the mixture of all four regioisomers, mainly on the basis of chemical shifts and signal patterns of the bridgehead protons in the ¹H NMR spectrum, as already described for the unsubstituted regiomer dimers **2a**.⁵ Due to the symmetry of the four dimers **2**, the bridgehead protons display two doublets with a characteristic coupling constant of $J = 11$ Hz for the head-to-tail dimers *syn*-**ht-2** and *anti*-**ht-2**, whereas these protons of the head-to-head dimers *syn*-**hh-2** and *anti*-**hh-2** exhibit singlets in their ¹H NMR spectra. The π - π interaction of the transannular aromatic rings results in small chemical shift differences of the bridgehead protons for the *syn* and *anti* isomers. In the *anti* isomers, the weak donor-acceptor interaction between the pyridinium and the benzo ring induces a partial decrease of positive charge at the quarternary nitrogen atom, which causes a slight high-field shift of the vicinal bridgehead proton 6-H compared to the *syn* isomers. Further confirmation of the *anti* structure of the isolated dimers was obtained by ROESY-NMR experiments, in which a NOE interaction between the proton pairs 1-H/7'-H and 4-H/10'-H was unambiguously shown. The transannular interaction between the aromatic rings becomes evident by comparison of the isolated *anti* dimers⁸ *anti*-**ht-2a,c,d,e,f**; thus, the proton signals of the pyridinium ring are significantly shifted to higher field with increasing π -donor strength of the substituent at the opposite phenyl moiety.

The regioselectivity of the solid-state photoreaction of acridizinium salts **1c·Br**, **1d·Br**, and **1e·ClO₄** may be explained by a favorable arrangement of the chro-

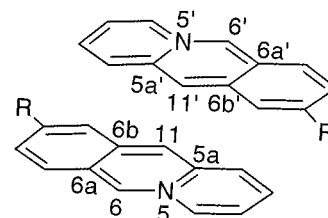


Figure 2. Atom numbers in acridizinium salts **1** used for the definition of the angles α - δ .

mophores in the crystalline state. The two acridizinium partners are facing each other in a *anti*-head-to-tail arrangement to avoid electrostatic repulsion between the positively charged quarternary nitrogen atoms and between the π -donor-substituted benzo rings; in addition, this geometrical arrangement facilitates attractive electronic interactions between the donor and acceptor functionalities. Moreover, the photoinertness of some solid samples may be caused by a large separation between the reaction centers of two acridizinium salts. Due to the restricted freedom of movement in the constrained crystalline medium, the two destined molecules cannot approach each other close enough for photodimerization.

X-ray structure analyses were performed with the selected samples **1c·Br**, **1c·BF₄**, and **1d·Br** to verify the proposed solid-state arrangements of the acridizinium salts (Figure 1).

In the case of the photoactive derivatives **1c·Br** and **1d·Br**, the crystal lattice consists of pairs of chromophores that seem to be well-arranged for *anti*-head-to-tail dimerization. Within the crystal lattice of the solid salt **1c·BF₄** there is also a close pair of arenes; however, there exists no appropriate orientation of the two molecules for unhindered photodimerization. Furthermore, within the crystal lattice of the salt **1c·BF₄**, two acridizinium molecules face each other in a *syn*-head-to-head arrangement. The distances d and d' between the opposite reactive *meso* positions (i.e., C-6 and C-11), which form the new C-C bonds in the photodimerization, were taken as structural parameters for a quantitative comparison of the solid-state structures. The deviation from an ideal superposed position of two molecules was quantified according to the data presented by Jones and Wang^{4b} in terms of the angles α , β , γ , and δ , with $\alpha = \text{C6-C11-C6'}$, $\beta = \text{C11'-C6'-C11}$, $\gamma = \text{N5-C6a-C5a'}$, and $\delta = \text{C6b'-C5a'-C6a}$ for acridizinium salts **1c·Br** and **1d·Br** and $\alpha = \text{C6-C11-C11'}$, $\beta = \text{C6'-C11'-C11}$, $\gamma = \text{N5'-C6a'-C6a}$, and $\delta = \text{N5-C6a-C6a'}$ for salt **1c·BF₄** (numbering according to Figure 2). The ideal d value was deduced from earlier results of structure-reactivity correlations for the solid-state dimerization of anthracenes and alkenes,⁹ and the best values for α , β , γ ,

(8) The ¹H NMR spectroscopic data of the isolated dimers *anti*-**ht-2a,f** have already been reported, see refs 5 and 7.

(9) Ramamurthy, V. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH Publishers: New York, 1991; p 133.

Table 1. Structural Parameters of the Solid-State Arrangement of the Acridizinium salts **1c·Br, **1c·BF₄**, and **1d·Br** Obtained from X-ray Structure Analysis**

	<i>d</i> (pm)	<i>d'</i> (pm)	α (deg)	β (deg)	γ (deg)	δ (deg)
1c·Br	388.6	388.6	100.7	79.3	112.4	68.1
1d·Br	378.2	378.2	108.7	71.3	93.4	85.7
1c·BF₄	620.7	620.7	102.8	77.2	144.7	35.3

and δ result from the proposal that the π -orbital lobes of the reactive *meso* carbon atoms of the two molecules should have a maximum overlap. Thus, the ideal structural parameters for the photodimerization should be $d = d' < 400$ pm, with $\Delta d = 0$ pm, and $\alpha = \beta = \gamma = \delta = 90^\circ$.

The observed structural features of compounds **1c·Br**, **1c·BF₄**, and **1d·Br** resemble those of the acridizinium salts **1a** and **1b**.^{4b,10} Although the distance between the reaction centers is suitable for the photoreactive acridizinium salts **1c·Br** and **1d·Br**, the solid-state arrangements of these compounds exhibit small deviations from the ideal angles α , β , γ , and δ (Table 1). The two acridizinium molecules need to move within the crystal in order to align for the dimerization process. Despite this required motion, the solid-state photodimerization of the salts **1c·Br** and **1d·Br** does proceed in the crystal. Thus, it may be concluded that a deviation from two perfectly superimposed molecules is tolerated as long as the *meso* positions of two molecules are separated by a distance smaller than ca. 400 pm; however, the movement that is required for the dimerization presumably causes a destructive phase transition in the crystal, so that a topotactic single-crystal-to-single-crystal transformation is not observed.¹¹

In the case of the photoinert salt **1c·BF₄** the distances d and d' and the angles γ and δ deviate significantly from the appropriate parameters and photodimerization is no longer possible. Moreover, within the crystal lattice of salt **1c·BF₄**, the two closest acridizinium molecules face each other in a distorted *syn*-head-to-head arrangement, a new feature for acridizinium salts. It may be assumed that this orientation also results from an intermolecular attractive donor–acceptor interaction between one pyridinium moiety and one chloro-substituted benzene ring that are separated by only 360 pm, which is comparable to the sum of the van der Waals radii of two carbon atoms (340 pm).

Although no X-ray structure analyses were performed for all of the acridizinium salts, we deduce from these results and the previously reported solid-state structures of compounds **1a** and **1b**⁴ that the arrangement of the salts **1d·ClO₄**, **1e·ClO₄**, **1f·Br**, and **1f·ClO₄** in the solid state correlates with their photoreactivity in analogy to the structure–reactivity relationship, which has been established for the salts **1c·Br**, **1d·Br**, and **1c·BF₄**. It is noteworthy, that the amino-substituted acridizinium salt

1f is photoinert in the solid state irrespective of the counteranion. Due to its relatively strong donor substituent it was expected that this system should have a higher tendency to organize in the *anti*-head-to-tail arrangement. It may be assumed that in this case the arrangement in the solid state is governed by hydrogen bonds of the amine functionality, which dominate the donor–acceptor interplay and lead to a solid-state arrangement that is unfavorable for photodimerization.

Since it was shown that the regioselectivity of the solid-state photodimerization of acridizinium salt **1d·Br** is not influenced by the way the solid samples were prepared, it is concluded that the donor–acceptor interplay, which was observed in the single crystal of **1d·Br** (crystallized from methanol/ethyl acetate), is also effective in the polycrystalline phase of this compound. It is important to emphasize that in the case of the parent structure **1a** only the irradiation of single crystals gave exclusively the *anti*-head-to-tail photoproduct,^{4a} whereas polycrystalline samples led to all possible dimers.⁵ The role of the counterions in the solid-state photochemistry has not been investigated in detail in these studies; nevertheless, it is evident that the small bromide counterion does not disturb the photoactivity, whereas the larger perchlorate and tetrafluoroborate ions slow the reaction or, in some cases, even prevent it in the solid state.

Conclusion

In summary, it was shown that the solid-state irradiation of appropriately tailored 9-donor-substituted acridizinium salt derivatives gives rise to a highly regioselective and quantitative photodimerization. This is not observed in the solution photolysis and may be used for synthetic purposes; moreover, single crystals are not necessarily required for this selective transformation. The regioselectivity is explained in terms of a favorable alignment of two molecules in the crystalline state, which is governed by π -donor–acceptor interactions. This advantageous molecular feature should prove promising in the application of this concept to other donor–acceptor-substituted arene- and heteroarene-type chromophores for regiomericly controlled [4+4] photocycloadditions in the solid state.

Experimental Section

General Information. NMR spectra were recorded in DMSO-*d*₆ (¹H 200 MHz; ¹³C 50.3 MHz; ROESY ¹H 600 MHz). Elemental analyses were performed by Mr. C.-P. Kneis at the University of Würzburg, Institute of Inorganic Chemistry. Melting points are uncorrected.

Acridizinium salts **1b–e** were synthesized according to reported procedures.^{7,12,13} Anion exchange was achieved according to Hünig et al.¹⁴ Although, some of the acridizinium salts are known, there are only limited NMR data available; therefore, these data are also provided in this paper.

Photolysis in Solution and in the Solid State. The solution photolyses were performed in deoxygenated acetonitrile or methanol with a 150-W mercury high-pressure lamp (Heraeus TQ 150). Solid-state irradiations were carried out at 10 °C with the crystalline samples crushed between Pyrex slides in argon-

(10) Some geometric parameters of the compounds **1a** and **1b** with varying anions have been reported, but the actual crystallographic data have not been published so far; see ref 4.

(11) For single-crystal-to-single-crystal photoreactions, see: (a) Leibovitch, M.; Olovsson, G.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1998**, *120*, 12755. (b) Suzuki, T.; Fukushima, T.; Yamashita, T. *J. Am. Chem. Soc.* **1994**, *116*, 2793. (c) Enkelmann, V.; Wegner, G.; Novak, K. Wagener, K. B. *J. Am. Chem. Soc.* **1993**, *115*, 10390. (d) Ohashi, Y. *Acc. Chem. Res.* **1988**, *21*, 268. (e) Reference 4a. (f) Hasegawa, M. *Chem. Rev.* **1983**, *83*, 507. (g) Thomas, J. M. *Nature* **1981**, *289*, 633. (h) Thomas, J. M.; Morsi, S. E.; Desvergne, J. P. *Adv. Phys. Org. Chem.* **1977**, *15*, 63. (i) Wegner, G. *Pure Appl. Chem.* **1977**, *49*, 443. (j) Schmidt, G. M. *Pure Appl. Chem.* **1971**, *27*, 647.

(12) Earley, W. G.; Dority, J. A., Jr.; Kumar, V.; Mallamo, J. P. *Heterocycles* **1995**, *41*, 309.

(13) Bradsher, C. K.; Sherer, J. P.; Parham, J. H. *J. Chem. Eng. Data* **1965**, *10*, 180.

(14) (a) Gries, W.-K.; Günther, E.; Hünig, S. *Liebigs Ann.* **1991**, 1021. (b) Geuder, W.; Hünig, S. *Angew. Chem.* **1983**, *85*, 501; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 489.

flushed polyethylene bags or by distributing the ground solid on the inner walls of an NMR tube. The photolysate was analyzed by means of ^1H NMR spectroscopy. In preparative runs the solid samples (20–100 mg) were placed in a flask (Duran glassware) and flushed with argon. During photolysis the flask was frequently removed and placed in a sonic bath for 1–2 min. Full conversion was indicated by complete bleaching of the sample. Analysis of the product by ^1H NMR spectroscopy showed the quantitative formation of the dimers **anti-2-ht** without any byproduct.

X-ray Crystallography. All data were collected from shock-cooled crystals on an Enraf-Nonius CAD4 four circle diffractometer (graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 71.073$ pm) equipped with a low-temperature device.¹⁵ A semiempirical absorption correction was employed for structures **1c-Br** and **1d-Br**.¹⁶ The structures were solved by direct methods (SHELXS-97¹⁷) and refined by full-matrix least-squares methods against F^2 (SHELXL-97¹⁸). R values: $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{0.5}$, $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2, 0) + 2F_c^2]$. **1c-Br**: $\text{C}_{13}\text{H}_{11}\text{BrClNO}$, triclinic, space group $P1$, $Z = 2$, $a = 722.23(10)$ pm, $b = 963.95(13)$ pm, $c = 1031.25(14)$ pm, $\alpha = 108.927(11)^\circ$, $\beta = 93.748(9)^\circ$, $\gamma = 111.432(11)^\circ$, $V = 0.6182(2)$ nm³, $\rho_c = 1.679$ Mg m⁻³, 3219 reflections measured, 1610 unique, $R_1[I > 2\sigma(I)] = 0.0210$, $wR_2(\text{all data}) = 0.0540$, $g_1 = 0.0296$, $g_2 = 0.3741$ for 162 parameters and 2 restraints. **1c-BF₄**: $\text{C}_{13}\text{H}_9\text{BClF}_4\text{N}$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 620.73(9)$ pm, $b = 1070.79(8)$ pm, $c = 1903.2(3)$ pm, $\beta = 96.085(7)^\circ$, $V = 1.2579(3)$ nm³, $\rho_c = 1.592$ Mg m⁻³, 1902 reflections measured, 1756 unique, $R_1[I > 2\sigma(I)] = 0.0286$, $wR_2(\text{all data}) = 0.0821$, $g_1 = 0.0492$, $g_2 = 0.4226$ for 227 parameters and 40 restraints. **1d-Br**: $\text{C}_{13}\text{H}_{11}\text{Br}_2\text{NO}$, triclinic, space group $P1$, $Z = 2$, $a = 723.2(3)$ pm, $b = 966.7(3)$ pm, $c = 1031.3(4)$ pm, $\alpha = 68.82(3)^\circ$, $\beta = 85.98(2)^\circ$, $\gamma = 68.39(3)^\circ$, $V = 0.6233(4)$ nm³, $\rho_c = 1.902$ Mg m⁻³, 3241 reflections measured, 1622 unique, $R_1[I > 2\sigma(I)] = 0.0333$, $wR_2(\text{all data}) = 0.0907$, $g_1 = 0.0637$, $g_2 = 0.5312$ for 163 parameters and 109 restraints. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms (bonded to oxygen atoms of water molecules) were located by difference Fourier syntheses and refined isotropically with O–H distance restraints. All other hydrogen atoms of the molecules were assigned ideal positions and refined isotropically using a riding model with U_{iso} constrained to 1.2 times the U_{eq} of the parent atom. The BF_4 anion in compound **1c-BF₄** is disordered and was refined to a split occupancy of 0.5/0.5 using distance and similarity restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-120565 (**1d-Br**), CCDC-120566 (**1c-Br**), and CCDC-120567 (**1c-BF₄**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (internat.) + 44(1223)336-033; e-mail deposit@ccdc.cam.ac.uk].

1c-Br: mp 249–251 °C (dec). Anal. Calcd for $\text{C}_{13}\text{H}_9\text{BrClN}\cdot\text{H}_2\text{O}$: C, 49.95; H, 3.59; N, 4.36. Found: C, 49.95; H, 3.55; N, 4.48. **1c-BF₄**: mp 211–213 °C (dec); ^1H NMR 8.04–8.17 (m, 3 H), 8.21–8.25 (m, 3 H), 9.23 (s, 1 H), 9.37 (d, $J = 7$ Hz, 1 H), 10.53 (s, 1 H); ^{13}C NMR: δ 122.7, 123.9, 124.3, 125.7, 126.9, 130.6, 131.9, 131.9, 134.6, 135.2, 138.1, 139.6, 140.9. Anal. Calcd

for $\text{C}_{13}\text{H}_9\text{BClF}_4\text{N}$: C, 51.79; H, 3.01; N, 4.65. Found: C, 51.71; H, 3.02; N, 4.66.

1d-ClO₄:¹³ mp 222–224 °C (dec) (lit.: 218–220 °C). **1d-Br**:¹³ mp 265–267 °C (dec) (lit.: 262–263 °C); ^1H NMR: 8.04–8.21 (m, 3 H), 8.51 (d, $J = 9$ Hz, 1 H), 8.68 (d, $J = 9$ Hz, 1 H), 8.82 (s, 1 H), 9.24 (s, 1 H), 9.40 (d, $J = 7$ Hz, 1 H), 10.61 (s, 1 H); ^{13}C NMR: δ 122.6, 123.7, 124.2, 126.9, 128.9, 129.1, 130.1, 131.8, 134.1, 134.4, 135.7, 138.0, 140.6.

1e-ClO₄:¹² ^1H NMR 4.16 (s, 3 H), 7.75 (dd, $J = 9$ Hz, 2 Hz, 1 H), 7.78 (s, 1 H), 7.88 (dd, $J = 8$ Hz, 6 Hz, 1 H), 8.07 (dd, $J = 9$ Hz, 7 Hz, 1 H), 8.46–8.53 (m, 2 H), 8.96 (s, 1 H), 9.20 (d, $J = 6$ Hz, 1 H), 10.29 (s, 1 H).

1f-Br: mp 270–272 °C (dec). Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{BrN}_2\cdot 0.5\text{H}_2\text{O}$: C, 54.95; H, 4.26; N, 9.86. Found: C, 54.37; H, 3.95; N, 9.61. **1f-ClO₄**: mp 232–233 °C (dec); ^1H NMR: δ 7.01 (d, $J = 2$ Hz, 1 H), 7.46–7.54 (m, 2 H), 7.75 (dd, $J = 9$ Hz, 7 Hz, 1 H), 8.12 (d, $J = 9$ Hz, 1 H), 8.21 (d, $J = 9$ Hz, 1 H), 8.40 (s, 1 H), 8.85 (d, $J = 7$ Hz, 1 H), 9.83 (s, 1 H); ^{13}C NMR δ 99.9, 116.6, 118.2, 120.2, 124.9, 125.2, 129.4, 130.5, 133.3, 137.3, 138.2, 138.5, 154.8. Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{ClN}_2\text{O}_4$: C, 52.98; H, 3.76; N, 9.51. Found: C, 52.67; H, 3.48; N, 8.85.

anti-ht-2c: mp 295–300 °C (dec); ^1H NMR δ 6.14 (d, $J = 11$ Hz, 2 H), 7.09 (d, $J = 11$ Hz, 2 H), 7.46 (dd, $J = 8$ Hz, 2 Hz, 2 H), 7.56 (d, $J = 8$ Hz, 2 H), 7.64 (d, $J = 2$ Hz, 2 H), 8.09 (dd, $J = 8$ Hz, 6 Hz, 2 H), 8.29 (d, $J = 7$ Hz, 2 H), 8.58 (dd, $J = 8$ Hz, 7 Hz, 2 H), 9.31 (d, $J = 6$ Hz, 2 H); ^{13}C NMR: δ 49.1, 70.7, 126.5, 128.7, 128.9, 129.1, 129.8, 133.4, 133.9, 134.5, 146.3, 147.2, 152.4. Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{Br}_2\text{Cl}_2\text{N}_2\cdot 2\text{H}_2\text{O}$: C, 49.95; H, 3.59; N, 4.36. Found: C, 50.05; H, 3.56; N, 4.58.

anti-ht-2d: mp 300–305 °C (dec); ^1H NMR δ 6.17 (d, $J = 11$ Hz, 2 H), 7.06 (d, $J = 11$ Hz, 2 H), 7.53 (d, $J = 8$ Hz, 2 H), 7.62 (dd, $J = 8$ Hz, 2 Hz, 2 H), 7.85 (d, $J = 2$ Hz, 2 H), 8.07 (dd, $J = 8$ Hz, 6 Hz, 2 H), 8.23 (d, $J = 7$ Hz, 2 H), 8.57 (dd, $J = 8$ Hz, 7 Hz, 2 H), 9.26 (d, $J = 6$ Hz, 2 H); ^{13}C NMR δ 49.1, 70.7, 122.5, 126.5, 129.1, 130.0, 131.7, 131.7, 133.6, 134.6, 146.4, 147.2, 152.4. Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{Br}_2\text{N}_2\cdot 2\text{H}_2\text{O}$: C, 43.73; H, 3.11; N, 3.92. Found: C, 43.54; H, 3.08; N, 3.95.

anti-ht-2e: ^1H NMR δ 4.17 (s, 6 H) 6.04 (d, $J = 11$ Hz, 2 H), 6.91 (dd, $J = 8$ Hz, 3 Hz, 2 H), 6.95 (d, $J = 11$ Hz, 2 H), 7.14 (d, $J = 3$ Hz, 2 H), 7.44 (d, $J = 8$ Hz, 2 H), 8.08 (dd, $J = 8$ Hz, 7 Hz, 2 H), 8.17 (d, $J = 7$ Hz, 2 H), 8.52 (dd, $J = 8$ Hz, 7 Hz, 2 H), 9.18 (d, $J = 7$ Hz, 2 H); ^{13}C NMR δ 50.1, 55.6, 71.2, 113.7, 114.8, 126.2, 126.3, 128.8, 129.1, 134.1, 146.1, 146.7, 153.3, 159.7.

Acknowledgment. This work was generously financed by the *Fonds der Chemischen Industrie* and the *Bundesministerium für Bildung und Forschung*. Constant encouragement and generous support by Prof. W. Adam is gratefully appreciated. We would like to thank E. Ruckdeschel for the recording of ROESY-NMR spectra and Prof. S. Hünig for helpful discussions. This paper is dedicated to Prof. Dr. John R. Scheffer, University of British Columbia, on the occasion of his 60th birthday.

Supporting Information Available: Thermal ellipsoids (50%) of the asymmetric units, packing diagrams, and full crystallographic data of compounds **1c-Br**, **1c-BF₄**, and **1d-Br** including crystal data, bond lengths and angles, atomic coordinates, and anisotropic thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO990465B

(15) Stalke, D. *Chem. Soc. Rev.* **1998**, 27, 171.

(16) North, A. C. T.; Philipps, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, 24, 351.

(17) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, 46, 467.

(18) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*. University of Göttingen, 1997.