# Ground and Excited State Aromatic−Aromatic Interactions with Distance Control by Hydrogen Bonding[†]

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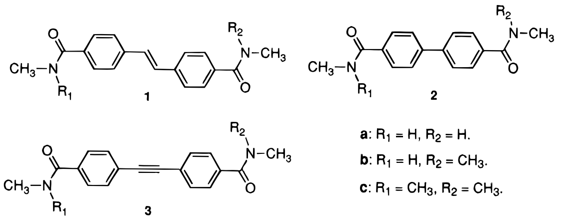
The structures of the dimers and aggregates formed between aromatic molecules in the ground and excited states are a subject of continuing interest.[1−5] Theoretical modeling of the benzene dimer suggests that the face-to-face dimer has an optimum center-to-center distance of ca. 3.8 Å, whereas the edge-to-face dimer has an optimum center-to-center distance of 5 Å.[2,3] Ground state dimer structure has a profound effect on the photochemical behavior of excited dimers.[4,5] Face-to-face dimers typically display strongly perturbed excimer-like fluorescence and may undergo photodimerization, whereas edge-to-face dimers display weakly perturbed exciton-like fluorescence and do not photodimerize. Schmidt and co-workers[6] found that chlorination of stilbene and several other arylolefins can result in face-to-face crystal packing with a short axis of 4 Å, as a consequence of attractive intrastack Cl−Cl interactions.[7] Thus 2,4-dichlorostilbene displays excimer fluorescence at low temperature and photodimerizes at higher temperature.[6b] In contrast, stilbene-fuctionalized phospholipids are proposed to adopt edge-to-face geometries in Langmuir−Blodgett assemblies or vesicles.[5] These assemblies display exciton-like fluorescence.

Secondary amide derivatives of both alkane- and arenedicarboxylic acids are frequently found to crystallize with 5 Å translation-related hydrogen-bonded secondary structures (Figure 1a).[8,9] The up−down translational arrangement of amide-amide hydrogen bonding provides a molecular scaffold which permits investigations of arene−arene interactions at a fixed distance of 5 Å. We report here the preliminary results of our investigation of the crystal packing and solid state photochemical behavior of secondary diamides **1a**−**3a** and of the association and fluorescence of the secondary−tertiary diamides **1b** and **2b** in organic solvents. These results indicate that amide−amide hydrogen bonding favors an edge-to-face geometry for neighboring arenes. Comparison of the fluorescence spectra of **1a**−**3a** in the solid state with those of **1b** and **2b** in organic solvents further suggests that these arenedicarboxamides adopt similar structures in solution and the solid state.



**a**: $R_1$ = H, $R_2$ = H.
**b**: $R_1$ = H, $R_2$ = $CH_3$.
**c**: $R_1$ = $CH_3$, $R_2$ = $CH_3$.

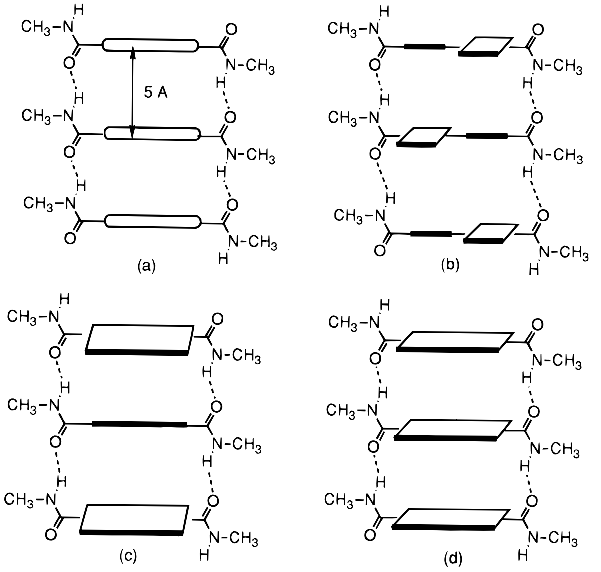


**Figure 1.** Schematic representations of (a) the 5 Å translational axis created by optimum amide−amide hydrogen bonding, (b) a hydrogen-bonded tape of stilbene or biphenyl diamides **1a** and **2a**, (c) a hydrogen-bonded tape of diamide **3a**, and (d) a hypothetical face-to-face hydrogen-bonded tape for **2a** or **3a**.

The arenedicarboxamides were synthesized from the corresponding dicarboxylic acids by standard procedures and recrystallized from mixed solvents.[10,11] The crystal structures of **1a**−**3a** conform to the translational-packing motif of Figure 1a.[12] The individual stilbenedicarboxamide molecules in **1a** are nonplanar and noncentrosymmetric with a phenyl−phenyl dihedral angle of 28.1° and phenyl−amide dihedral angles of 37.6° and 24.8°. Hydrogen-bonded pairs of molecules have the same 28.1° dihedral angle between phenyl planes separated by 4.95 Å. This packing arrangement is shown schematically in Figure 1b. The crystal structure of the biphenyldicarboxamide **2a** has inter- and intramolecular phenyl−phenyl dihedral angles of 35.5° with phenyl planes separated by 4.92 Å. The crystal structure of **3a** has a dihedral angle of 67.9° between adjacent planar diphenylacetylenediamides separated by 5.05 Å, as shown schematically in Figure 1c.

The separation between hydrogen-bonded pairs of diamides in **1a-3a** corresponds to the optimum amide hydrogen-bonded structure.[8,9] The interplane dihedral angle of 67.9° in **3a** is near the maximum in the distribution of phenylalanine−phenylalanine dihedral angles observed for globular proteins.[13] Since

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[†] Dedicated to Marshall Gates, scientist, teacher, editor, on the occasion of his 80th birthday.

(1) (a) Janda, K. C.; Hemminger, J. C.; Winn, J. S.; Novick, S. E.; Harris, S. J.; Klemperer, W. *J. Chem. Phys.* **1975**, *63*, 1419. (b) Steed, J. M.; Dixon, T. A.; Klemperer, W. *J. Chem. Phys.* **1979**, *70*, 4940. (c) Law, K. S.; Schauer, M.; Bernstein, E. R. *J. Chem. Phys.* **1984**, *81*, 8471. (d) Muehldorf, A. V.; Engen, D. V.; Warner, J. C. Hamilton, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 6561. (e) Arunan, E.; Gutowsky, H. S. *J. Chem. Phys.* **1993**, *98*, 4294. (f) Laatikainen, R.; Ratilainen, J.; Sebastian, R.; Santa, H. *J. Am. Chem. Soc.* **1995**, *117*, 11006.

(2) (a) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990,** *112*, 4768. (b) Hunter, C. A.; Sanders, J, K. M. *J. Am. Chem. Soc.* **1990,** *112*, 5525. (c) Bartell, L. S.; Shi, X. *J. Phys. Chem.* **1988,** *92*, 5667. (d) Pettersson, I.; Liljefors, T. *J. Comput. Chem.* **1987,** *8*, 1139.

(3) (a) Linse, P. *J. Am. Chem. Soc.* **1992**, *114*, 4366. (b) Linse, P. *J. Am. Chem. Soc.* **1993**, *115*, 8793.

(4) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587.

(5) (a) Song, X.; Perlstein, J.; Whitten, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 7816. (b) Song, X.; Geiger, C.; Leinhos, U.; Perlstein, J.; Whitten, D. G. *J. Am. Chem. Soc.* **1994**, *116*, 10340.

(6) Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 2014. (b) Cohen, M. D.; Green, B. S.; Ludmer, Z.; Schmidt, G. M. J. *Chem. Phys. Lett.* **1970**, *7*, 486.

(7) For a review see: Venkatesan, K.; Ramamurthy, V. In *Photochemistry in Organized and Constrained Media;* Ramamurthy, V., Ed.; VCH: New Yrok, 1991.

(8) Leiserowitz, L.; Tuval, M. *Acta Crystallogr.* **1978**, *B34*, 1230.

(9) Garcia-Tellado, F.; Geib, S. J.; Goswami, S.; Hamilton, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 9265.

(10) (a) Lee, B. H.; Marvel, C. S. *J. Polym. Sci. Chem. Ed.* **1982**, *20*, 393. (b) Burdett, K. A. *Synthesis* **1991**, 441. (c) Salunkhe, M.; Wu, T.; Letsinger, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 8768.

(11) Reaction of the stilbenedicarboxylic acid with a 1:1 mixture of methyl- and dimethylamine yielded a ca. 1:2:1 mixture of **1a**, **1b**, and **1c**, from which **1b** was obtained by fractional crystallization. **2b** was prepared analogously.

(12) Crystallographic data were obtained at −120 ± 1 °C using an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation. The following are data for the crystal system, space group, color, unit cell parameters (Å and deg), *Z*, *R*, $R_w$, and GOF: (**1a**) monoclinic, $P2_1/c$, colorless, $a = 9.889(2)$, $b = 22.248(3)$, $c = 6.970(2)$, $\beta = 102.85(2)$, 4, 0.041, 0.035, 1.64. (**2a**) monoclinic, $P2_1/c$, colorless, $a = 9.831(4)$, $b = 19.812\ (4)$, $c = 7.049(2)$, $\beta = 101.40(2)$, 4, 0.050, 0.039, 1.82. (**3a**) triclinic, $P\bar{1}$, colorless, $a = 5.853(2)$, $b = 8.417(4)$, $c = 17.354(5)$, $\alpha = 118.14(3)$, $\beta = 94.51(3)$, $\gamma = 98.26(4)$, 2, 0.036, 0.037, 2.02.

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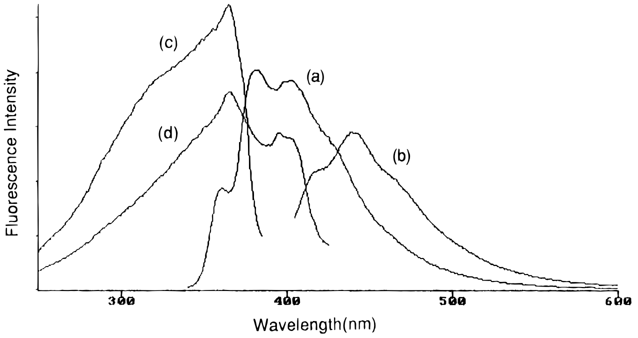

**Figure 2.** Fluorescence emission spectra of a single crystal of **1a** excited at (a) 320 and (b) 395 nm and fluorescence excitation spectra with emission monitored at (c) 402 and (d) 440 nm.

the crystal structure of **3a** could readily accommodate a face-to-face geometry (Figure 1d), the preference for the edge-to-face geometry plausibly reflects the greater stabilization energy for the edge-to-face vs face-to-face geometry when the interplane separation is fixed at 5 Å, as is the case for the benzene dimer.[1−3] The interplane dihedral angles for **1a** and **2a** are smaller than that of **3a**, about halfway between the optimized edge-to-face and face-to-face geometries. In the case of the biphenyl **2a**, an "optimized" edge-to-face geometry could be obtained for biphenyl intramolecular dihedral angles of either 0° (Figure 1c) or 90° (Figure 1b). The estimated energy differences between planar or perpendicular biphenyl and twisted biphenyl are ~2 kcal/mol.[14] It is interesting to note that unsubstituted *trans*-stilbene and biphenyl are planar in the solid state, but nonplanar in the vapor or solution phase.[15,16] The dihedral angles of **1a** and **2a** in the solid state are similar to those of the parent molecules in solution.

There is no evidence to indicate that the attractive intrastack Cl−Cl interactions responsible for face-to-face crystal packing of 2,4-dichlorostilbene persist in organic solvents. In contrast, diamides can form hydrogen-bonded dimers and higher aggregates in solution.[17] The secondary diamides **1a**−**3a** are highly insoluble in chloroform due to extended hydrogen-bonding. The secondary−tertiary diamides **1b** and **2b** are appreciably more soluble and have dimerization constants of 11 and 4 dm$^3$ mol$^{-1}$, estimated from NMR titration and dilution data using the method of Dimicloi and Hélène.[18] The concentration dependence of the aromatic proton chemical shifts indicates that **1b** and **2b** form head-to-tail dimers, but does not distinguish between face-to-face and edge-to-face geometries.

As noted above, the photochemical behavior of excited dimers is strongly dependent upon their ground state geometries. The fluorescence spectra of a single crystal of **1a** and acetonitrile solutions of **1b** are shown in Figures 2 and 3, respectively. Excitation of either **1a** or **1b** near the first absorption band maximum results in fluorescence similar in appearance to that of a highly dilute solution. Excitation in the red edge of the absorption band results in red-shifted fluorescence emission and a red-shifted fluorescence excitation spectrum, as expected for exciton splitting in an edge-to-face dimer.[19] Increasing the concentration of **1b** results in a decrease in intensity of monomer emission and an increase in dimer emission (Figure 3). The ditertiary amide **1c**, which cannot form hydrogen-bonded dimers, displays only monomer fluorescence even at high concentrations. Analysis of the fluorescence decays of **1b** in acetonitrile solution provides singlet lifetimes of ≤0.2 ns for the monomer and 0.9 ns for the dimer. Crystals of **1a** fail to undergo either photodimerization or photoisomerization upon prolonged irradiation. The absence of photodimerization is consistent with the large center-to-center distance between adjacent stilbenes.[7] Irradiation of acetonitrile solutions of **1b** at the long wavelengths used to excite exciton fluorescence (Figure 3) results in much more efficient photoisomerization than photodimerization. The similar fluorescence emission spectra for long-wavelength excitation of a single crystal of **1a** and concentrated solutions of **1b** and the absence of efficient photodimerization suggest that the hydrogen-bonded dimer of **1b** adopts a ground state structure similar to that of **1a** in the crystal.

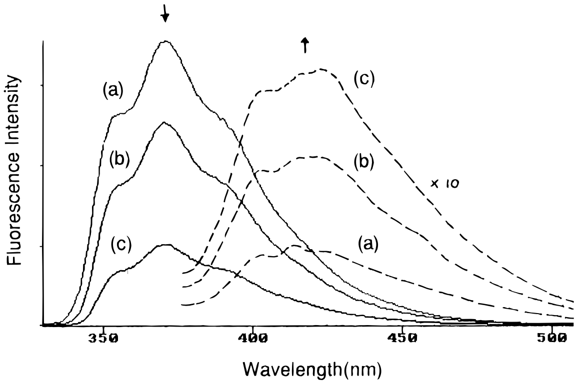

**Figure 3.** Fluorescence spectra of **1b** in acetonitrile solution: (a) 1.7 × 10$^{-5}$ M, (b) 4.0 × 10$^{-5}$ M, (c) 5.7 × 10$^{-5}$ M. Excitation wavelengths are 320 (full curves) and 366 nm (broken curves).

In summary, we find that amide−amide hydrogen bonding of the arenedicarboxamides **1a**−**3a** in the solid state and **1b** and **2b** in acetonitrile solution results in a ground state edge-to-face geometry for adjacent arene chromophores. An edge-to-face geometry has also been proposed for organized assemblies of stilbene-containing phospholipids, which have fluorescence spectra and decay times similar to those of **1b** in acetonitrile solution.[5] In contrast, the stilbene dimer formed upon duplex formation between complementary oligonucleotides containing stilbenedicarboxamide chromophores in aqueous solution displays excimer fluorescence and efficient photodimerization.[20] This behavior is analogous to that of 2,4-dichlorostilbene, which possesses a face-to-face geometry in the solid state.[6b] Thus the fluorescence of dimers and aggregates of aromatic hydrocarbons in solution may provide information about their ground state structures. The relationship between ground state structure and photochemical behavior in hydrogen-bonded dimers and aggregates is under continuing investigation.

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**Supporting Information Available:** ORTEP drawings of molecular structures and the crystal-packing motifs, tables of positional and thermal parameters, bond lengths and bond angles, and crystallographic data for **1a**−**3a** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) (a) Burley, S. K.; Petsko, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 7995. (b) Singh, J.; Thornton, J. M. *FEBS Lett.* **1985**, *191*, 1.

(14) Takei, Y.; Yamaguchi, T.; Osamura, Y.; Fuke, K.; Kaya, K. *J. Phys. Chem.* **1988**, *92*, 577.

(15) (a) Hoekstra, A.; Meertens, P.; Vos, A. *Acta Crystallogr.* **1975**, *B31*, 2813. (b) Traetteberg, M.; Frantsen, E. B.; Mijlhoff, F. C.; Hoekstra, A. *J. Mol. Struct.* **1975**, *26*, 57.

(16) (a) Hargreaves, A.; Hasan Rizvi, S. *Acta Crystallogr.* **1962**, *15*, 365. (b) Rubio, M.; Merchán, M.; Ortí, E.; Roos, B. O. *Chem. Phys. Lett.* **1995**, *234*, 373.

(17) (a) Dado, G. P.; Desper, J. M.; Gellman, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 8630. (b) Nadin, A.; Derrer, S.; McGeary, R. P.; Goodman, J. M.; Raithby, P. R.; Holmes, A. B.; O'Hanlon, P. J.; Pearson, N. D. *J. Am. Chem. Soc.* **1995**, *117*, 9768.

(18) Dimicoli, J.-L.; Hélène, C. *J. Am. Chem. Soc.* **1973**, *95*, 1036.

(19) (a) Cantor, C. R.; Schimmel, P. R. *Biophysical Chemistry-Part II: Techniques for the Study of Biological Structure and Function:* W. H. Freeman and Company: New York, 1980; pp 390−480. (b) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals.* Clarendon Press: Oxford, 1982; Chapter 1.

(20) Lewis, F. D.; Wu, T.; Burch, E. L.; Bassani, D. M.; Yang, J.-S.; Schneider, S.; Jäger, W.; Letsinger, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 8785.