Unusually Short (C−H···π) Hydrogen Bonds for Effective Supramolecular (Aromatic/Aromatic) Organization in Edge-to-Face Motifs

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For the creation of new supramolecular structures in the organic solid state,[1] there is increasing interest in different types of stable aromatic/aromatic bonding motifs—of which there are two basic classes extant with either face-to-face (cofacial)[2] or edge-to-face (perpendicular)[3] orientation. The latter is particularly interesting in that the intermolecular interaction between aromatic donor/acceptor pairs can be envisaged as a (carbon)*hydrogen bond to a π-center*.[4] To optimize such aromatic/aromatic interactions for crystal engineering, we envisaged the cooperative use of a phenyl C−H donor bearing a positive charge in conjunction with a phenyl acceptor bearing a negative charge to strengthen the hydrogen bond by charge assistance.[5] As such, we now report on arylated cation/anion pairs comprising a novel series of highly colored arenediazonium tetraphenylborate salts [$ArN_2^+BPh_4^-$] with exceptionally short (C−H···π) hydrogen bonds, as determined by X-ray crystallography and defined by the pair of geometrical parameters shown below.[6]

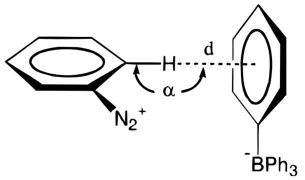
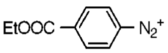
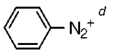
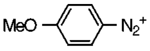


Table 1. Hydrogen-Bonding Parameters for C−H···π Association in Crystalline Arenediazonium Tetraphenylborates[a]

ArN_2^+	d,[b] Å	α,[c] deg	motif
	2.496	156.2	ion pairs
 [d]	2.358−2.536	162.7−169.0	ion pairs
	2.241−2.349	157.9−171.0	cyclic (ion)
	2.441−2.570[e]	144.8−145.1[e]	quadruplets
	(2.784−2.874)[f]	(115.6−137.4)[f]	(3-d network)
	2.408, 2.411	159.3, 162.4	ionic chains

[a] C−H bond lengths normalized to the neutronographic value of 1.083 Å for *ortho* protons, unless indicated otherwise. [b] H···i (centroid). [c] C−H···i (centroid). [d] Based on six nonequivalent units in two crystal structures. [e] *Para* hydrogens. [f] *Meta* hydrogens.

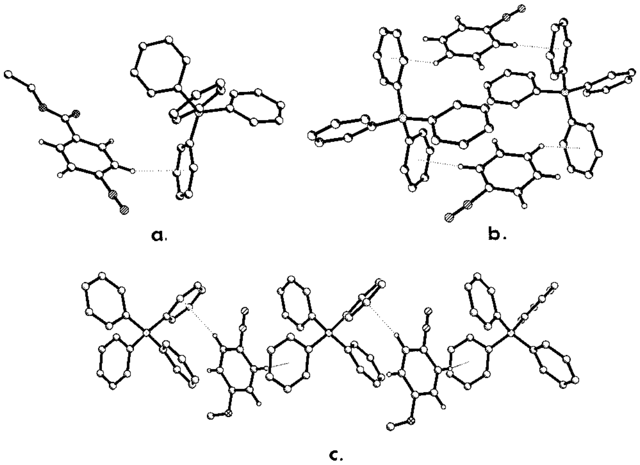


Figure 1. Hydrogen-bonding motifs in crystalline tetraphenylborate salts of (a) *p*-carbethoxy-, (b) unsubstituted, and (c) *p*-methoxybenzenediazonium as ion pairs, cyclic (ion) quadruplets, and linear ionic chains, respectively.

Thus, Table 1 lists hydrogen bonds as short as d = 2.2 Å, particularly for the *ortho* protons on the ArN_2^+ acceptors. When the hydrogen bond is taken to the phenyl centroid of the BPh_4^- donor, the angle α is ~160°. Such strong hydrogen-bonding motifs lead to the three basic structural units illustrated in Figure 1. Thus the ion-pair structure in (a) involves a single *ortho* hydrogen in the ArN_2^+ acceptor that is directed to the phenyl centroid of Ph_4B^-, and it is a persistent feature in all crystal structures. When a pair of *ortho* hydrogens are equally involved, the linear ionic chain (c) threads through the crystal. The involvement of the weaker *para* hydrogen bonds leads to the cyclic (ion) quadruplet (b). It is particularly noteworthy that the unsubstituted benzenediazonium acceptor (PhN_2^+) utilizes all three types of hydrogens (including *meta*)[7] to form the interesting 3-dimensional hydrogen-bonded network presented in Figure 2.

Strong (C−H···π) interactions are inherent to all the supramolecular assemblies listed in Table 1. Importantly, such C−H···π

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(1) (a) *The Crystal as a Supramolecular Entity*; Desiraju, G. R., Ed.; Wiley: Chichester, NY, 1996. (b) *Comprehensive Supramolecular Chemistry*; Atwood, J. L., et al., Eds.; Pergamon: New York, 1996; Vol. 1−11. (c) Subramanian, S.; Zavorotko, M. J. *Coord. Chem. Rev.* **1994**, *137*, 357. (d) Aakeröy, C. B. *Acta Crystallogr.* **1997**, *B53*, 569. (e) Toda, F. In *Advances in Supramolecular Chemistry*; Gokel, G. W., Ed.; JAI Press: London, 1992; Vol. 2, pp 141−192.

(2) (a) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.*, **1990**, *112*, 5527. (b) Desiraju, G. R.; Gavezzotti, A. *J. Chem. Soc., Chem. Commun.* **1989**, 621. (c) Gavezzotti, A. *Chem. Phys. Lett.* **1989**, *161*, 67. (c) Dance, I.; Scudder, M. *New J. Chem.* **1998**, 481.

(3) (a) Malone, J. F.; Murray, C. M.; Charlton, M. H.; Docherty, R.; Lavery, A. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3429. (b) Cochran, J. E.; Parrott, T. J.; Whitlock, B. J.; Whitlock, H. W. *J. Am. Chem. Soc.* **1992**, *114*, 2269.

(4) (a) Jakubetz, W.; Schuster, P. *Tetrahedron* **1971**, *27*, 101. (b) Viswamitra, M. A.; Radhakrishnan, R.; Bandekar, J.; Desiraju, G. R. *J. Am. Chem. Soc.* **1993**, *115*, 4868. (c) Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. *Tetrahedron* **1995**, *51*, 8665.

(5) Braga, D.; Grepioni, F.; Tedesco, E. *Organometallics* **1998**, *17*, 2669. Note that charge assistance for hydrogen bonding in aromatic−aromatic interactions is maximized in cation/anion pairs, and less so in ion/neutral pairs. For neutral/neutral interactions, see: Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768.

(6) (a) The distance d is taken to the phenyl centroid (i) of BPh_4^- and α is the (C−H···i) angle. (b) Crystal data for p-$MeOC_6H_4N_2^+BPh_4^- \cdot {}^1/_2PhCMeCH_2$: monoclinic, $P2_1/n$, at −150 °C, a = 11.3186(1) Å, b = 16.4446(2) Å, c = 15.3768(1) Å, β = 96.185(1)°, V = 2845.42(5) Å^3, Z = 4, R [$wR(F^2)$] = 0.0549 (0.1349) on 8223 unique reflections with $I > 2\sigma(I)$, GOF = 1.03, 353 parameters refined. Crystal data for $PhN_2^+BPh_4^- \cdot {}^1/_2OCMe_2$: triclinic, $P\bar{1}$, at −150 °C, a = 9.8947(2) Å, b = 15.9444(3) Å, c = 17.2787(1) Å, α = 78.666(1)°, β = 84.800(1)°, γ = 74.330(1)°, V = 2571.44(8) Å^3, Z = 4, R [$wR(F^2)$] = 0.0618 (0.1235) on 7945 unique reflections with $I > 2\sigma(I)$, GOF = 1.06, 631 parameters refined. Crystal data for $PhN_2^+BPh_4^- \cdot {}^1/_2CH_2I_2$: triclinic, $P\bar{1}$, at −150 °C, a = 9.9740(1) Å, b = 21.2237(3) Å, c = 26.0147(1) Å, α = 83.859(1)°, β = 81.932(1)°, γ = 83.204(1)°, V = 5391.2(1) Å^3, Z = 8, R [$wR(F^2)$] = 0.0779 (0.1660) on 16625 unique reflections with $I > 2\sigma(I)$, GOF = 1.19, 1259 parameters refined. Crystal data for p-$EtO_2CC_6H_4N_2^+$-BPh_4^-: monoclinic, $P2_1/c$, at −150 °C, a = 9.5861(1) Å, b = 14.4626(2) Å, c = 20.2227(4) Å, β = 99.375(1)°, V = 2766.23(7) Å^3, Z = 4, R [$wR(F^2)$] = 0.0485 (0.0927) on 4585 unique reflections with $I > 2\sigma(I)$, GOF = 1.06, 459 parameters refined. Siemens SMART diffractometer equipped with CCD detector and N_2 low-temperature device (LT-2), λ(Mo Kα) = 0.71073 Å; computer programs: SHELXS-86 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), SHELXL-93 (Sheldrick, G. M. *Program for the Refinement of Crystal Structures*, Universität Göttingen, 1993), and SHELXTL PLUS (*Structure Determination System*, V. 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994).

(7) The relative C−H···π distances of $d \simeq$ 2.3, 2.5, and 2.8 Å for the hydrogen bonds from the *ortho*, *para*, and *meta* protons, respectively, follow the same trend in their electron densities[9] (as a measure of their relative acidities).

10.1021/ja982945a CCC: $15.00

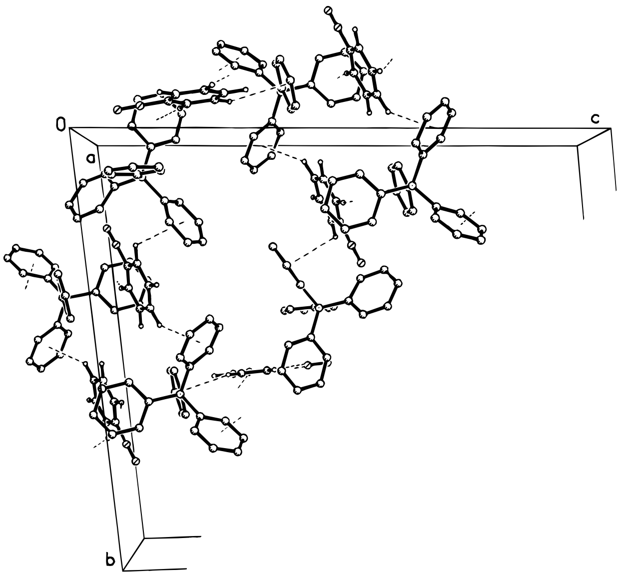

Figure 2. Repeating unit built by multiple C−H$\cdots\pi$ interactions in the structure of benzenediazonium tetraphenylborate. The 3-dimensional hydrogen-bonded network derives from its extension along the *x*-axis (and inversion/translation in the *yz*-plane).

interactions cannot merely result from crystal packing since the same hydrogen-bonding motif is present in the four different crystal structures of $ArN_2^+BPh_4^-$ (comprised of eight structurally independent units). Indeed, the extended 3-dimensional network in Figure 2 shows how strong (C−H$\cdots\pi$) bonds to *ortho*, *para*, and *meta* hydrogens in ArN_2^+ can dominate the crystal assembly for effective solid-state engineering.

We attribute the unusually short (C−H$\cdots\pi$) hydrogen bonds found in arenediazonium tetraphenylborates to the felicitous confluence of (a) the pronounced electron-acceptor properties of the cationic ArN_2^+ and (b) the enhanced electron-donor properties of the anionic BPh_4^-. Thus the "acidic" character of the *ortho* hydrogens was first reported in the pioneering X-ray crystallographic analysis of benzenediazonium chloride by Römming[8] which is strongly supported by our electron-density measurements[9] and the theoretical calculations by Glaser.[10] Indeed, the very short C−H$\cdots\pi$ distance of $d = 2.24$ Å in Table 1 is even comparable to that found for the strongly acidic hydrogen halides, such as $d = 2.25$ Å[11] for F−H$\cdots\pi$ in the hydrogen fluoride/benzene complex (in the gas phase), and $d = 2.345$ Å[12] for Cl−H$\cdots\pi$ in the hydrogen chloride analogue (in crystals). Further, the anionic BPh_4^- as an excellent electron donor is an effective base in hydrogen bonding, as demonstrated by Bakshi et al. with alkylammonium and pyridinium salts.[13,14]

The donor/acceptor interaction inherent to arenediazonium tetraphenylborates is also manifested by their vivid colors (Table 2), which derive from charge-transfer transitions arising from intermolecular $\pi-\pi$ interactions of the phenyl groups in Ph_4B^- with the cationic ArN_2^+ in the bathochromic order: *p*-EtO_2C− > H > *p*-MeO−.[15] Together with the highly directed (C−H$\cdots\pi$) hydrogen bonding in Table 1, such delocalized charge-transfer interactions can be readily modulated by substituent effects on ArN_2^+ (as well as substituents on BPh_4^-)—sufficient to satisfy the two principal criteria for effective crystal engineering.[16]

Table 2. Charge-Transfer ($\pi-\pi$) Interactions in Arenediazonium Tetraphenylborates

	diazonium substituent		
interaction	*p*-MeO	H	*p*-EtO_2C
Ar/Ph^a		3.4−3.5 Å	
N/Ph^b	3.18 Å	2.97−3.11 Å (2.96−3.01 Å)	3.12 Å (3.04 Å)
color	yellow	orange	dark red
stability	2 h (23 °C)	1 h (23 °C)	2 min (0 °C)

[a] $\pi-\pi$ interaction in ArN_2^+/BPh_4^- ion pairs with a tilt of 6−16°. [b] Nitrogen−π distance of diazonium terminus to the phenyl group in BPh_4^- with a tilt of 1−6° or (in parentheses) N−π distance with a tilt of 16−41°.

Although the unusually short hydrogen bond of $d = 2.24$ Å between phenyl groups, as found in this study, is unique to benzenediazonium tetraphenylborates, there are other examples of rather short C−H$\cdots\pi$ distances.[17] However, even the shortest C−H$\cdots\pi$ contacts with $d < 2.4$ Å in the tetraphenylborates[17] have heretofore not been generally recognized as hydrogen bonds since the structures were reported without explicit reference to such unusually close interactions. As such, our findings will now allow us to employ the charge-assistance concept in a more general sense by anticipating the deliberate design of cationic/anionic components as an effective strategy for strong hydrogen bonding via edge-to-face interactions of aromatic donor/acceptor pairs.

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Supporting Information Available: X-ray structural data and tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for *p*-$EtOOCC_6H_4N_2^+BPh_4^-$, $PhN_2^+BPh_4^-\cdot{}^1/_2CH_2I_2$, $PhN_2^+BPh_4^-\cdot{}^1/_2OCMe_2$, and *p*-$MeOC_6H_4N_2^+BPh_4^-\cdot{}^1/_2PhCMeCH_2$ (35 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[8] (a) Römming, C. *Acta Chem. Scand*. **1963**, *17*, 1444. See also: (b) Cygler, M.; Przybylska, M.; Elofson, R. M. *Can. J. Chem*. **1982**, *60*, 2852.

[9] Electron-density measurements on crystalline *m*-nitrobenzenediazonium tetrafluorobrate indicate the buildup of electrostatic charge of +0.17, +0.12, and +0.11 electrons on the *ortho*, *para*, and *meta* hydrogens, respectively (unpublished results). The corresponding theoretical values on the isolated benzenediazonium cation are +0.114, +0.106, and +0.103 electrons.[10]

[10] Glaser R.; Horan, C. J. *J. Org. Chem.* **1995**, *60*, 7518. Further indications of such interionic hydrogen bonding even in solution derive from the concentration-dependent (upfield) chemical shifts of the aromatic protons in *p*-Me and *p*-$MeOC_6H_4N_2^+BPh_4^-$ (see: Kosynkin, D. Ph.D. Dissertation, University of Houston, August, 1997). Compare Cochran et al. in ref 3b and the following: Cloninger, M. J.; Whitlock, H. W. *J. Org. Chem.* **1998**, *63*, 6153.

[11] Balocchi, F. A.; Williams, J. H.; Klemperer, W. *J. Phys. Chem.* **1983**, *87*, 2079.

[12] Deeg, A.; Mootz, D. *Z. Naturforsch.* **1993**, *48B*, 571. In the gas phase see: Read, W. G.; Campbell, E. J.; Henderson, G. *J. Chem. Phys.* **1983**, *78*, 3501.

[13] (a) Bakshi, P. K.; Linden, A.; Vincent, B. R.; Roe, S. P.; Adhikesavalu, D.; Cameron, T. S.; Knop, O. *Can. J. Chem.* **1994**, *72*, 1273. (b) Bakshi, P. K.; Cameron, T. S.; Knop, O. *Can. J. Chem.* **1996**, *74*, 201. See also: (c) Braga, D.; Grepioni, F.; Tedesco, E. in ref 5. For other examples of X−H$\cdots\pi$ hydrogen bonds, see: (d) Atwood, J. L.; Hamada, F.; Robinson, K. D.; Orr, G. W.; Vincent, R. L. *Nature* **1991**, *349*, 683. (e) Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Science* **1992**, *257*, 942. (f) Kim, K. S.; Lee, J. Y.; Choi, H. S.; Kim, J.; Jang, J. H. *Chem. Phys. Lett.* **1997**, *265*, 497.

[14] In the classical theory of hydrogen bonding in X−H$\cdots$B, "B must be a good electron donor but not necessarily a highly electronegative group", see: Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, 1960; p 202ff. The classical point of view on these interactions is that they are "largely ionic in character" (Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1948; p 284).

[15] Such a trend relates to the charge-transfer transition ($h\nu_{CT}$) of arenediazonium acceptors with other types of aromatic donors. See: Bockman, T. M.; Kosynkin, D.; Kochi, J. K. *J. Org. Chem.* **1997**, *62*, 5811.

[16] Compare: (a) Hanton, L. R.; Hunter, C. A.; Purvis, D. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1134. (b) Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 630.

[17] Of the more than 1000 tetraphenylborate structures reported in the Cambridge Crystallographic Database (CCD), a few *pyridinium*-type structures have C−H$\cdots\pi$ distances as short as $d < 2.4$ Å but none as short as 2.2 Å. For the phenyl-type structures reported herein, there is a single example of a cationic phenylphosphine complex of cobalt acetate with $d = 2.3$ Å (not reported). See: Asam, A.; Huttner, G.; Serau, V.; Zsolnai, L. *Chem. Ber.* **1994**, *127*, 501. Note that the statistical search[5] of CCD for edge-to-face motifs in aromatic/aromatic interactions in general reveals most C−H $\cdots\pi$ contacts to be $d = 2.79(2)$ Å.