≡CH··π *versus* ≡CH···Halogen interactions—the crystal structures of the 4-halogenoethynylbenzenes

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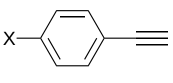
The crystal structures of the 4-halogenoethynylbenzenes are quite similar and exhibit ≡CH···π interactions, whereas the structure of 4-fluoroethynylbenzene has very interesting and rare intermolecular ≡CH···F contacts.

The X-ray crystal structures of 1,4-dihalogenobenzenes (α-form of 1,4-dichlorobenzene) are, for the most part, isomorphous;[1–6] notable exceptions are the structures of 1,4-diiodobenzene[7] and those which contain fluorine.[8] For mixed 1,4-dihalogenobenzenes a disorder was found such that the positions of the ring carbon atoms are almost fixed, but the sites of the halogens are crystallographically equivalent.[1,9] The packing motif typically found in 1,4-dihalogenobenzenes is a zigzag pattern of intermolecular X··X interactions.

Fluorine containing compounds, however, crystallize differently.[8] Fluorine often plays a special role in that it is expected not to exhibit intermolecular F··F contacts. We recently reported the crystal structures of a series of ethynylated benzenes in which ≡CH··π interactions predominated.[10] Combining both moieties (halogen and ethynyl group) in a single benzene derivative might lead to a deeper insight into the intermolecular interactions of the ethynyl group.

Accordingly we present the crystal structures of the 4-X-ethynylbenzenes (with X = F **4**, Cl **1**, Br **2** and I **3**).† The X-ray structures of compounds **1**, **2** and **3** are isomorphous. The cell dimensions are quite similar and remarkably also comparable to those of the 1,4-dihalogenobenzenes. The packing motif of **1** is easy to surmise: the molecules form a layer structure in the *bc* plane similar to that observed in the α-form of 1,4-dichlorobenzene,[2–4] in 1,4-dibromobenzene,[5] and also in 1,4-diethynylbenzene.[10,11] The molecules are tilted by 32.7° out of this plane (Fig. 1) and are held together by attractive ≡CH··π and Cl··Cl contacts, both of which dominate the packing. This geometry of T-shaped ≡CH··π hydrogen bridges is known from other alkynes,[12] as well as the zigzag pattern of the terminal chlorine atoms (*e.g.* in the α-form of 1,4-dichlorobenzene[2–4]). The ≡CH··π contacts to the center of the triple bond are quite short whereas the intermolecular Cl··Cl distances are relatively long (Table 1) but still have a significant attractive character.



1 X = Cl
2 X = Br
3 X = I
4 X = F

Molecules **2** and **3** are disordered in the same manner as the mixed 1,4-dihalogenobenzenes: the center of inversion is in the center of the disordered ring system. This means that if the disorder is resolved 50% of the 1- and 4-positions of the benzene ring are occupied by the halogen atom and 50% by the ethynyl group (Fig. 2). Nevertheless, the packing motifs are the same as in **1** or in the 1,4-dihalogenobenzenes with the same zigzag pattern at the two ends of the molecules. For bromide **2**, two different positions of the ring system could be found and refined. The intermolecular interactions that determine the crystal packing are ≡CH··π and X··X. Hydrogen bridges between the ethynyl hydrogen atom to bromine or iodine might exist if statistical disorder is assumed; however, this is not very likely because the resulting ≡CH··X distances are much shorter than the sums of the van der Waals radii ($d_{\mathrm{H\cdots Br}}$ = 243.9, Σ_{vdW} = 299; $d_{\mathrm{H\cdots I}}$ = 238.9, Σ_{vdW} = 314 pm[13]). This indicates that the disorder is not statistical; instead there exists a disorder in which ordered domains or layers within the lattice are statistically distributed in the crystal.

Table 1 Selected intermolecular geometric parameters of compounds **1**–**3**[a]

Comp.	d(X–X)/pm	∠(C–X··X)(°)	d(≡CH··M)/pm	∠(≡CH··M)(°)
1	379.0	92.5	357.9	171.9
2	386.7	96.1	266.9	173.6
3	394.9	97.0	255.7	174.9

[a] M represents the center of the triple bond, X the halogen atoms. The positions of the hydrogen atoms were normalized to a C–H distance of 108 pm.

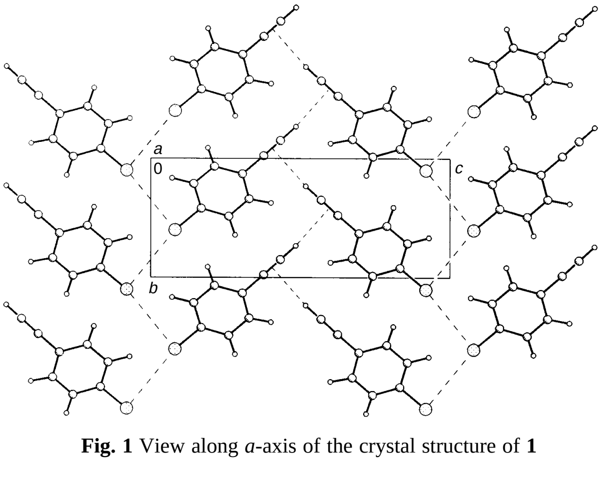


Fig. 1 View along *a*-axis of the crystal structure of **1**

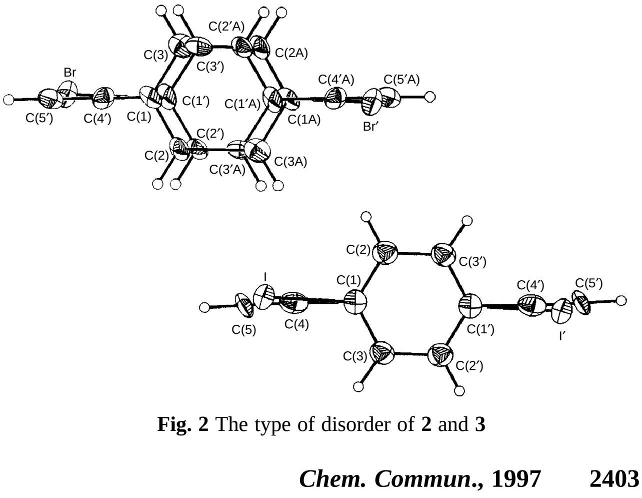


Fig. 2 The type of disorder of **2** and **3**

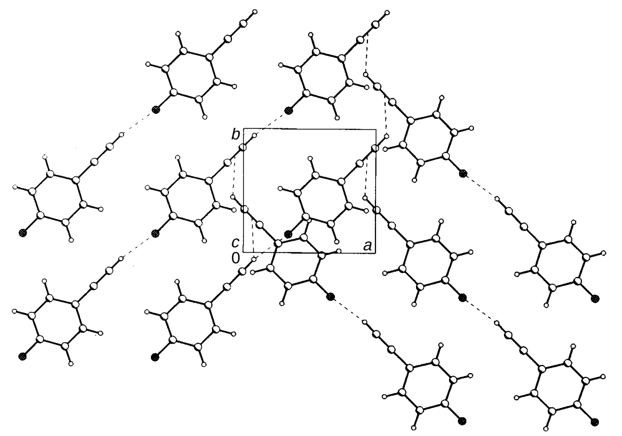


Fig. 3 The two interactions which dominate the packing in the structure of **4**

In contrast to the other systems, the packing of fluoride **4** is totally different, as is shown in Fig. 3. Two attractive forces dominate the arrangement. In both cases the ethynyl hydrogen atoms serve as hydrogen bridge donors. One acceptor is the triple bond, but this contact does not possess an ideal geometry: The ≡CH··π distance is comparatively long (307.6 pm) and the angle ≡C–H··π is rather small (129.4°). The other attractive contact is much more interesting: a hydrogen bond to covalently bound organic fluorine is very much disputed.[14,15] The ≡CH··F distance in **4** is 226.4 pm and thus is significantly shorter than the sum of the van der Waals radii (254 pm[13]). The ≡CH··F angle of 140.4° supports the assumption that a ≡CH··F hydrogen bridge exists, at least if the carbon atom is sp-hybridized. This is also sustained by the fact, that the packing of **4** is totally different compared to 4-halogenoethynylbenzenes **1**–**3**. Therefore we must conclude that the predominant interactions in **4** consist of ≡CH··F hydrogen bridges.

We gratefully acknowledge the DFG, the Fonds der Chemischen Industrie and the NSF for financial support of this work.

Footnotes and References

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† *Crystal data* for **1**: C_8H_5Cl (Aldrich), no recrystallization necessary, space group $P2_1$, $a = 3.881(3)$, $b = 5.811(4)$, $c = 14.455(9)$ Å, $\beta = 95.02(5)°$, $V = 324.7(4)$ Å^3, $Z = 2$, $D_c = 1.40$ g cm^{-3}, 1016 unique reflections $F_o > 4\sigma(F_o)$, 102 parameters, $2\theta_{max} = 60°$, $R1 = 0.039$.

For **2**: C_8H_5Br,[16] crystals obtained by sublimation; space group $P2_1/c$, $a = 3.941(1)$, $b = 5.827(2)$, $c = 14.779(4)$ Å, $\beta = 94.57(2)°$, $V = 338.3(2)$ Å^3, $Z = 2$, $D_c = 1.78$ g cm^{-3}, 1065 unique reflections $F_o > 4\sigma(F_o)$, 87 parameters, $2\theta_{max} = 80°$, $R1 = 0.062$.

For **3**: C_8H_5I;[17] crystals obtained by sublimation; space group $P2_1/c$, $a = 4.046(1)$, $b = 5.888(2)$, $c = 15.322(5)$ Å, $\beta = 93.63(3)°$, $V = 364.3(2)$ Å^3, $Z = 2$, $D_c = 2.08$ g cm^{-3}, 1255 unique reflections $F_o > 4\sigma(F_o)$, 64 parameters, $2\theta_{max} = 70°$, $R1 = 0.052$.

For **4**: C_8H_5F (Aldrich), no recrystallization necessary, space group $P2_1/c$, $a = 7.065(3)$, $b = 6.587(3)$, $c = 13.241(6)$ Å, $\beta = 99.65(3)°$, $V = 607.5(4)$ Å^3, $Z = 4$, $D_c = 1.31$ g cm^{-3}, 1529 unique reflections $F_o > 4\sigma(F_o)$, 103 parameters, $2\theta_{max} = 60°$, $R1 = 0.055$.

All measurements were performed on a Nicolet R3m/V X-ray four circle diffractometer at 125 K. Mo-Kα X-rays ($\lambda = 0.71073$ Å), graphite monochromator and the program SHELXTL[18] refined on F^2, H-atom positions taken from difference fourier maps and refined free and isotropically. CCDC 182/650.

1 A. Koug, *Nature*, 1947, **160**, 570.
2 U. Croatto, S. Bezzi and E. Bua, *Acta Crystallogr.*, 1952, **5**, 825.
3 G. L. Wheeler and S. D. Colson, *J. Chem. Phys.*, 1976, **65**, 1227.
4 C. Panattoni, E. Frasson and S. Bezzi, *Gazz. Chim. Ital.*, 1963, **93**, 813.
5 A. Maiga, Nguygen-Ba-Chanh, Y. Haget and M. A. Cuevas-Diatre, *J. Appl. Crystallogr.*, 1984, **17**, 210.
6 D. Britton, *Acta Crystallogr., Sect. B*, 1976, **32**, 976.
7 A. Hinchliffe, R. W. Munn, R. G. Pritchard and C. J. Spicer, *J. Mol. Struct.*, 1985, **130**, 93.
8 R. Boese, H.-Chr. Weiss and M. Kirchner, unpublished results.
9 S. B. Hendricks, *Z. Kristallogr.*, 1933, **84**, 85.
10 H.-Chr. Weiss, D. Bläser, R. Boese, B. M. Doughan and M. M. Haley, *Chem. Commun.*, 1997, 1703.
11 N. A. Ahmed, A. I. Kitaigorodskij and M. I. Sirota, *Acta Crystallogr.*, 1972, **28**, 2875.
12 For example, see T. Steiner, *J. Chem. Soc., Chem. Commun.*, 1995, 95; P. E. Eaton, E. Galoppini and R. Gilardi, *J. Am. Chem. Soc.*, 1994, **116**, 7588; R. K. McMullan, Å. Kvick and P. Popelier, *Acta Crystallogr., Sect. B*, 1992, **48**, 726.
13 R. S. Rowland and R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384.
14 J. A. K. Howard, V. J. Hoy, D. O'Hagan and G. T. Smith, *Tetrahedron*, 1996, **38**, 12613.
15 J. D. Dunitz and R. Taylor, *Chem. Eur. J.*, 1997, **3**, 89.
16 R. P. Hsung, C. E. D. Chidsey and L. R. Sita, *Organometallics*, 1995, **14**, 4808.
17 1-Ethynyl-4-iodobenzene was prepared in two steps (84% yield) from the corresponding molecule where the terminal acetylene was protected as the trimethylsilyl derivative and the aryl iodide protected as a diethyltriazene using the procedures described in: J. Zhang, D. J. Pesak, J. L. Ludwick and J. S. Moore, *J. Am. Chem. Soc.*, 1994, **116**, 4227.
18 G. M. Sheldrick, SHELXTL, Program for Crystal Structure Solution and Refinement, University of Göttingen, 1993.

Received in Cambridge, UK, 9th September 1997; 7/06564G