

## Intermolecular contacts and supramolecular motifs involved in the crystal packing of 9

The molecule possesses several functional groups able to behave as acceptors/donors relatively to O-H $\cdots$ O, O-H $\cdots$ N and C-H $\cdots$ F-C hydrogen bonding, C-Br $\cdots$ O halogen bonding and finally  $\pi$ - $\pi$  perfluoroarene/arene interactions. A detailed analysis of the intermolecular contacts below or close to the sum of van der Waals radii<sup>14</sup> has revealed the coexistence of a number of “classical” and non-classical interactions which give rise to slightly undulated 2D networks parallel to the ( $\bar{1}01$ ) crystallographic plane (Figure 2). First of all, the hydroxyl group of molecule B (O30-H30) acts as a hydrogen donor interacting through a bifurcated hydrogen bond either intermolecularly with the OH group of molecule A (O15-H15) and intramolecularly with nitrogen atom N16 (see Figures 1 and 2, and Supporting Information for details). Moreover, hydroxyl group O15-H15 of molecule A behaves as a bifurcated hydrogen bond donor towards acridine nitrogen atom N1 (intramolecular) and fluorine atom F18 belonging to molecule B (intermolecular). In fact, atom H15 is involved in a short intermolecular contact with the C18-F18 unit of molecule B and engaged in the “classical” O-H $\cdots$ O hydrogen bond already mentioned, thus forming a “three-center” hydrogen bond system<sup>15</sup> where a fluorine and a nitrogen atoms behave as acceptors (the C-F $\cdots$ H intermolecular contacts and their contribution to the crystal structure will be described later).

By means of the aforementioned described interactions, molecules A and B are held together in pairs in an almost coplanar fashion [dihedral angle between the molecular least-squares planes 11.75(3)°, r.m.s. deviation of fitted atoms of 0.0351 (molecule A) and 0.0180 Å (molecule B) by fitting all non-hydrogen atoms]. This dimeric building block, thought as a supramolecular motif, is further involved in intermolecular attractive interactions through halogen bonding<sup>16</sup>. Indeed, the bromine atom (Br4) of molecule A and the hydroxyl oxygen (O30) of molecule B' (belonging to the A'-B' dimer; see Figure 2 for definition of symmetry operations) give rise to Br $\cdots$ O halogen bonding. This is in line with the electron acceptor capability of carbon-bonded Cl, Br and I atoms (in order of increasing strength<sup>16a-c</sup>) in giving n $\rightarrow$  $\sigma^*$  Lewis complexes with O, S, N neutral electron

donors. In general, when the environment around the halogen is sufficiently electron-withdrawing, the resulting C-Hal $\cdots$ D (D = N, O, S) attractive interaction becomes strong enough to influence the crystal packing. In particular, with polyfluorinated alkyl and aryl halides, the halogen bond has been demonstrated either experimentally and theoretically to become significantly strong<sup>16</sup>. At the same time, it has been recognized that neutral and highly hybridized oxygen atoms (like  $sp^3$ ) behave as weak electron donors<sup>16c-e</sup>, a feature that in **9** is counterbalanced by an enhanced Lewis acidity of the bromine atom bonded to the electron withdrawing trifluoro-acridine moiety, making the Br $\cdots$ O interaction significant. The geometrical parameters for this interaction are the Br4 $\cdots$ O30' distance of 3.007(2) Å (sum of vdw radii<sup>14</sup> 3.37 Å) and the C4-Br4 $\cdots$ O30' angle of 164.78(13)°; the halogen bonding is in the direction of the C-Br axis (coherently with the anisotropic electron distribution around the bromine atom) and points towards the axis of the oxygen lone pair<sup>16</sup>. The paucity of structural data regarding the Br $\cdots$ O halogen bonding makes it difficult a statistically significant comparison with our data. The C-Br distance (1.867(4) Å) in **9** is only marginally affected by the halogen bonding, however it falls below the average value for C-Br bonds of the few structures based on areneF<sub>4</sub>Br fragments (mean 1.873(12), range 1.856-1.890 Å)<sup>17</sup>. Two examples of Br $\cdots$ O halogen bonding concern crystals of 3,5-dibromo-2-(2,4-dibromo-phenoxy)-phenol<sup>18</sup> (Br $\cdots$ O 3.015 Å) and 4-methoxy-2-carboxy-1,3,5-tribromo-benzene<sup>19</sup> (Br $\cdots$ O 3.145 Å), both consisting of 1D supramolecular polymers. Our data well compare with 1,2-bis(4-pyridyl)ethane/1,4-dibromo-tetrafluoro-benzene cocrystal<sup>16f</sup> containing Br $\cdots$ N halogen bonded linear chains (3.025(10) Å) and exhibiting a C-Br distance of 1.860(8) Å. Thus, this kind of intermolecular interaction gives a substantial contribution to the crystal packing. In addition, the halogen bonds connect the A-B “dimeric” units building a slightly undulated ribbon which extends along the [010] direction (Figure 2). It is worth mentioning here that the chain of hydrogen and halogen bonds developing along [010] are reflected in the highly anisotropic shrinking of the unit cell parameters with temperature<sup>20</sup>, *i.e.* the least contraction is observed for *b* (-0.04%) compared to *a* (-1.16%) and *c* (-1.25%) with a -2.21% for the unit cell volume on moving from 298 to 123 K.

The bromine atoms are also involved in slightly attractive interactions with several aromatic hydrogen atoms<sup>21</sup>; Br4 is at 3.13 and 3.15 Å from H12' and H27', respectively, whilst Br19 is at 3.22 Å from H27' (sum of vdw radii<sup>14</sup> 3.05 Å). These weaker interactions give a contribution to the structural cohesion of the crystal even if the aforementioned more intense interactions are the major entries to the lattice energy and may be involved in the self-recognition processes during the nucleation steps of crystals of **9**.

Analysis of the intermolecular contacts in **9** also reveals the presence of C-F $\cdots$ H-C interactions based on the favorable side by side arrangement of donors and acceptors belonging to adjacent [010] ribbons. In general, C-F $\cdots$ H interactions are weak and not able to play a dominant role in determining the crystal packing<sup>22</sup>. However, by analyzing the crystal structures of compounds containing C, H and F atoms only, a strict similarity between classical C-H $\cdots$ X (X = O, N) systems and bond patterns found for C-F $\cdots$ H-C crystals has emerged<sup>23</sup>. In our case, assuming as significant C-F $\cdots$ H interactions lying within the cutoff limit of 2.8 Å, two such contacts involving acidic hydrogens are found, comprising a short 2.375 Å C-F $\cdots$ H contact (See Supporting Information; H atom positions not corrected to standard d(C-H) neutron value) similar to 2.36 Å observed for 1,2,4,5-tetrafluoro-benzene<sup>23</sup> (H atom positions corrected to standard d(C-H) neutron value). With the aid of the attractive C-F $\cdots$ H contacts the ribbons are linked together side by side to build a slightly corrugated two-dimensional network lying parallel to the ( $\bar{1}01$ ) plane.

Finally, the geometrical requirements for the intermolecular interactions so far described, are fully compatible with an almost coplanarity between the molecules lying in each 2D sheet