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Intermolecular C—F···H—C contacts in the molecular packing of three isostructural *N*-(fluorophenyl)manno-pyranosylamines

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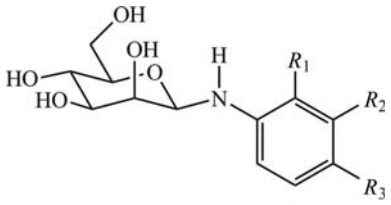
Among the three compounds reported here, namely *N*-(4-fluorophenyl)-β-D-mannopyranosylamine, (I), *N*-(3-fluorophenyl)-β-D-mannopyranosylamine, (II), and *N*-(2-fluorophenyl)-β-D-mannopyranosylamine, (III), all with chemical formula $C_{12}H_{16}FNO_5$, (I) and (II) are isostructural, whereas (III) assumes the same packing arrangement as the unfluorinated analogue *N*-phenyl-β-D-mannopyranosylamine, (IV), which has been reported previously. Similarities with respect to the intermolecular hydrogen-bonding patterns exist across the series (I)–(III). A packing motif that distinguishes the shared packing arrangement of (I) and (II) from that of (III) is a C—F···H—C chain of graph set *C*(4) that is preserved in the formal exchange of F and H atoms at the 4- and 3-positions on the aromatic ring of (I) and (II), but is replaced by a different chain of graph set *C*(5) when the F atom is located at the 2-position of the aromatic ring in (III). The steric role of the F atom in (I)–(III) is ambiguous but is examined here in detail.

Comment

The role played by covalently bonded fluorine in the solid-state packing of organic molecules is a topic of continuing active interest and is of direct relevance to the field of crystal engineering (Chopra & Guru Row, 2008; Zhu *et al.*, 2007; Reichenbächer *et al.*, 2005; Choudhury & Guru Row, 2004; Choudhury *et al.*, 2004, Brammer *et al.*, 2001), although whether solid-state interactions involving fluorine can actually be useful in the design and preparation of desired molecular packing motifs has been questioned in the literature. Previous studies have shown that the F atom of the C—F moiety is an exceptionally weak hydrogen-bond acceptor and that such interactions are significant only in particular cases, such as in those crystal structures from which stronger hydrogen-bonding groups are absent (Dunitz, 2004; Thalladi *et al.*, 1998; Dunitz & Taylor, 1997; Howard *et al.*, 1996). Solid-state halogen–halogen contacts between F atoms have been reported to be a consequence of molecular packing, rather than of attractive interactions that help determine that packing (Desiraju & Parthasarathy, 1989). Nevertheless, interactions of covalently bonded F atoms with neighboring H atoms, as well as with nearby π systems and with other halogen atoms, continue to be cited in the literature as factors that influence the packing of a variety of fluorine-bearing molecules, even in the presence of certain relatively strong hydrogen-bonding donors and acceptors (In *et al.*, 2003; Vangala *et al.*, 2002; Prasanna & Guru Row, 2000; Nangia, 2000).

Given this rather contradictory situation and the subtle nature of solid-state interactions involving C—F, we have been particularly interested in fluorine-substituted monosaccharide derivatives, which we have prepared and examined as part of our continuing study of the structures of the compounds formed upon reaction of monosaccharides with nitrogenous bases. We describe here the molecular and crystal structures of three fluorine-substituted glycosylamine derivatives of D-mannose, namely *N*-(4-fluorophenyl)-β-D-mannopyranosylamine, (I), *N*-(3-fluorophenyl)-β-D-mannopyranosylamine, (II), and *N*-(2-fluorophenyl)-β-D-mannopyranosylamine, (III).



(I) $R_1 = R_2 = H$, $R_3 = F$
(II) $R_1 = R_3 = H$, $R_2 = F$
(III) $R_2 = R_3 = H$, $R_1 = F$
(IV) $R_1 = R_2 = R_3 = H$

In general, the reaction of a monosaccharide with a nitrogenous base can yield as the crystalline product an open-chain Schiff base, as well as (or instead of) a cyclic glycosylamine. For example, we found in a previous study that D-mannose reacts with hydroxylamine to yield an open-chain oxime as the crystalline product (Ojala *et al.*, 2000). On the other hand, in related work we obtained glycosylamines, including the phenyl-substituted derivative, *N*-phenyl-β-D-mannopyranosylamine, (IV), rather than Schiff bases, from the reaction of D-mannose with aniline and its derivatives (Ojala *et al.*, 2000; Ojala, Ostman, Hanson & Ojala, 2001; Ojala, Ostman, Ojala & Hanson, 2001). We have now obtained the fluoro-substituted glycosylamines (I)–(III) by reaction of D-mannose with the corresponding fluoroanilines. In our previous studies, we found isostructuralism among certain glycosylamines, indicating that the solid-state hydrogen-bonding networks linking the monosaccharide moieties are sufficiently strong and extensive that even fairly drastic changes in the size, shape and even position of substitutents on the aryl ring may have little effect on them. For example, the *N*-4-bromophenyl, *N*-4-chlorophenyl, *N*-4-methylphenyl and *N*-3-chlorophenyl glycosylamines (Ojala *et al.*, 2000; Ojala, Ostman, Hanson &

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