3,4-Bis-O-propargyl-1,2:5,6-di-O-isopropylidene-D-mannitol: a study of multiple weak hydrogen bonds in the solid state

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The title homochiral compound, C_{18}H_{26}O_{6}, 1, was examined by single-crystal X-ray crystallography in order to understand its potential as a synthetic building block, particularly in inter- and intramolecular cyclocondensation reactions. It has also proven to be an excellent model for understanding multiple weak donor–acceptor D–H···A interactions involving terminal acetylenes as donors and as acceptors. The asymmetric unit of 1 comprises three almost identical independent molecules, each with the mannitol 2R,3R,4R,5R configuration and different conformations. Like independent molecules align in strands through acetylenic donor C–H···O contacts with equivalent dioxolanyl acceptor groups. Two of the strands are aligned unidirectionally, in parallel, while the third strand aligns perpendicular to the first two, to give interwoven layers in the supramolecular structure. A detailed study of the interdigitation of the second propargyl group from each independent molecule between strands, and of other short interstrand C–H···O contacts, provides new insight into the application of weak hydrogen-bond theory within the context of a conformationally flexible symmetrical molecule. Analyses of the Cambridge Structural Database using Crystal Packing Features and ConQuest search motifs support the importance of the D···A distance parameter, demonstrate the different influences of donor and acceptor types, and reveal the interplay between H···A and D···A contributions in different contact types.

1. Introduction

Propargyl groups are small and can serve as protection for alcohols that can be selectively removed in the presence of acetonides (1,3-dioxolanyls), methoxymethyl (MOM), benzyl and tert-butylmethylsilyl (TBS) ethers (Manabe et al., 2008; Rambabu et al., 2013), and provide subtle enhancement of diastereoselectivity in the synthesis of β-mannopyranosylated disaccharides (Crich et al., 2006). Propargyloxy groups can also undergo a variety of useful transformations in their own right. One of us recently described the synthesis of 3,4-bis-O-propargyl-1,2:5,6-di-O-isopropylidene-D-mannitol, 1, and its use in Cu^{I}-catalyzed dipolar cycloaddition reactions with n-alkyl azides to generate model compounds for potential new gemini surfactants (Mohammed et al., 2012), and extended this study in a collaborative effort to O-propargyl derivatives of glucose and galactose sugars and their reactions with polyfluoroalkyl azides as a route to novel fluorous surfactants (Ahmed et al., 2020). Related sugar-derived oligo-propargyl ethers have participated in intramolecular 1,3-dipolar nitrone addition (Ghorai et al., 2005) and been used as versatile building blocks in diversity-oriented synthesis of macrocycles (Maurya & Rana, 2017), while oligo-propargylated sugars and other polyols have been used with oligoazides in a modular
approach to neoglycoconjugates (Perez-Baldaras et al., 2009). Similar vicinal propargyl ethers derived from furfural have found use in conversion to bisphenols (Hashmi et al., 2007). Furthermore, dipropargyl malonate and terephthalate esters generate di- and tetranuclear clusters with cobalt, molybdenum and ruthenium metal ions (Zhang et al., 2001). In more tangential, although not exclusive, applications, cycloaddition reactions of bridged diacetylenic compounds have been used to generate a wide range of benzenoid substances, including fluoranthenes and indenocorannulenes (Wu et al., 2006), and propargylic enediyne alcohols have shown participation in nucleophilic cycloaromatization (Poloukhtine et al., 2010) akin to the important Bergman cyclization (Bergman, 1973). Relevant to these topics has been the lengthy and sometimes vexed discourse in the literature over the nature of C—H/C1/C1/C1O hydrogen bonds in crystals (Bernstein, 2013), where often the donor interactions of terminal acetylenic groups have been quoted. Matters of contention have been the acid strength and linearity of C—H/C1/C1/C1O hydrogen bonds (Desiraju, 1990, 1991), the distinction between weak attractive hydrogen bonds versus repulsive van der Waals interactions (Steiner & Desiraju, 1998, 1999; Schwalbe, 2012) and the attribution of contacts to electrostatics compared with van der Waals interactions (Steiner, 2002; Desiraju, 2002). Controversy over such matters has subsided (Bernstein, 2013), with an acceptance that in the solid state there is a continuum of these factors in research papers.

Table 1

| Crystal data
| Chemical formula | C18H26O6 |
| Mr | 338.39 |
| Crystal system, space group | Triclinic, P1 |
| Temperature (K) | 150 |
| a, b, c (Å) | 9.4726 (4), 10.3000 (5), 15.3583 (7) |
| α, β, γ (°) | 73.378 (2), 88.382 (2), 86.400 (2) |
| V (Å³) | 1432.94 (11) |
| Z | 3 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 0.09 |
| Crystal size (mm) | 0.24 × 0.21 × 0.19 |

Data collection

| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (SADABS; Bruker, 2016) |
| Tmin, Tmax | 0.679, 0.746 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 25389, 8343, 8134 |
| Rint | 0.028 |
| (sin θ/λ)max (Å⁻¹) | 0.595 |

Refinement

| R[F² > 2σ(F²)], wR(F²), S | 0.026, 0.065, 1.02 |
| No. of reflections | 8343 |
| No. of parameters | 661 |
| No. of restraints | 3 |
| H-atom treatment | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³) | 0.21, −0.15 |
| Absolute structure | Flack x determined using 3228 quotients [(F) − (F)]/[(F) + (F)] (Parsons et al., 2013) |
| Absolute structure parameter | 0.04 (17) |

Computer programs: APEX3 (Bruker, 2016). SAINT (Bruker, 2016), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b) and OLEX2 (Dolomanov et al., 2009).

Figure 1

(a) The molecular structure of title compound 1, showing the mannitol 2R,3R,4R,5R configuration. (b) The molecular structure of molecule A, showing the crystallographic atom-numbering scheme used throughout the remainder of the discussion, with displacement ellipsoids drawn with Mercury CSD (Version 3.0; Macrae et al., 2020) at the 40% probability level and H atoms shown as small spheres of arbitrary radius. (c) Overlay of molecules A (green), B (blue) and C (red) from the unit cell of compound 1 represented in capped sticks format, showing good overlap in the O1/O2 dioxolanyl portion (head) and significant variation, especially by molecule A, in the O5/O6 dioxolanyl portion (tail).

Table 1

| Experimental details. |
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play, and the best measure of weak donor–acceptor $D\cdots H\cdot\cdot\cdot A$ contact effectiveness is the $D\cdots A$ distance ($D$). Such considerations have influenced subsequent applications of weak hydrogen bonds to molecular recognition in organic crystals (Dunitz & Gavezzotti, 2005), virtual screening in drug design (Desiraju, 2005; Jones et al., 2012) and crystal engineering (Desiraju, 2013, Baillargeon et al., 2014).

As a homochiral vicinal bis-propargyl ether, substance 1 [Fig. 1(a)] therefore has potential to serve as a precursor for a wide range of intriguing materials whose function would depend largely upon tertiary structure and intermolecular interactions. Its solid-state structure also holds interest because of the close proximity of two notionally equivalent terminal acetylenic groups in the presence of two ethereal oxygen types (propargyloxy and dioxolanyl) as acceptors. The molecule was reprepared here and examined for the first time by single-crystal X-ray diffraction to ascertain a baseline for these structural features in the solid state.

2. Experimental

2.1. Synthesis

The synthesis of 3,4-bis-O-propargyl-1,2:5,6-di-O-isopropyridene-d-mannitol, 1 [systematic name: $(1R,2R)-1,2$-bis[$(R)$-2,2-dimethyl-1,3-dioxolan-4-yl]-1,2-bis(prop-2-yn-1-yl)oxy]ethane],

![Diagram](image-url)
has been reported (Mohammed et al., 2012) and the X-ray diffraction sample crystallized from EtOAc/n-hexane as colourless prisms (m.p. 50–52 °C).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The H atoms were not located in the difference Fourier map. Instead, the H atoms were placed geometrically and constrained according to their environment.

2.3. Analyses of the Cambridge Structural Database (CSD)

2.3.1. Searches of the CSD based on Mercury Crystal Packing Features (PFF). A total of 33 individual searches of the Cambridge Structural Database (CSD; Groom et al., 2016) for Crystal Packing Features (referred to here as PFFs) and illustrated in Fig. S1 (see supporting information) were carried out on 11 unique sets of donor D (A1, A2, B, C and D) and acceptor A (E, F, G, H, I and J) propargylic contacts that were recognised within the crystal structure of compound 1 (Fig. S2). Search criteria specified consideration of ‘Cyclicity’

Table 2

| Entry | Position | Torsions | Angle, ϕ (°) | A–C Mean, ϕ (°) (±deviation) |
|-------|----------|----------|--------------|-----------------------------|
| 1     | central  | C3A–C6A–C10A–C16A | −176.7 (2) | 180.0 (2.3) |
| 2     | central  | C3B–C6B–C10B–C16B | 175.2 (2)  | 180.0 (4.8) |
| 3     | central  | C3C–C6C–C10C–C16C | 175.5 (2)  | 180.0 (4.8) |
| 4     | head     | C2A–C3A–C6A–C10A | 76.6 (2)   | 78.7 (−2.1) |
| 5     | head     | C2B–C3B–C6B–C10B | 80.6 (2)   | 78.7 (1.9)  |
| 6     | head     | C2C–C3C–C6C–C10C | 78.9 (2)   | 78.7 (0.2)  |
| 7     | tail     | C6A–C10A–C16A–C15A | 85.0 (2)  | 77.4 (7.6)  |
| 8     | tail     | C6B–C10B–C16B–C15B | 73.8 (2)  | 77.4 (3.6)  |
| 9     | tail     | C6C–C10C–C16C–C15C | 73.3 (2)  | 77.4 (4.1)  |
| 10    | head     | O2A–C3A–C6A–C10A | 80.6 (2)   | −165.0 (2.1) |
| 11    | head     | O2B–C3B–C6B–C10B | 80.6 (2)   | −165.0 (1.6) |
| 12    | head     | O2C–C3C–C6C–C10C | 80.6 (2)   | −165.0 (0.6) |
| 13    | tail     | C6A–C10A–C16A–O5A | 159.5 (2) | −166.8 (7.3) |
| 14    | tail     | C6B–C10B–C16B–O5B | 170.2 (2) | −166.8 (3.4) |
| 15    | tail     | C6C–C10C–C16C–O5C | 170.6 (2) | −166.8 (3.8) |
| 16    | head     | C1A–O2A–C3A–C6A | 159.9 (2)  | −148.2 (−1.7) |
| 17    | head     | C1B–O2B–C3B–C6B | 159.9 (2)  | −148.2 (0.9) |
| 18    | head     | C1C–O2C–C3C–C6C | 142.4 (2)  | −148.2 (5.3) |
| 19    | tail     | C14A–O5A–C16A–C10A | 137.4 (2) | −137.9 (0.5) |
| 20    | tail     | C14B–O5B–C16B–C10B | 139.2 (2) | −137.9 (1.3) |
| 21    | tail     | C14C–O5C–C16C–C10C | 137.0 (2) | −137.9 (0.9) |
| 22    | head     | O3A–C6A–C10A–C16A | 52.4 (2)   | −58.2 (5.8) |
| 23    | head     | O3B–C6B–C10B–C16B | 61.4 (2)   | −58.2 (3.2) |
| 24    | head     | O3C–C6C–C10C–C16C | 60.8 (2)   | −58.2 (2.6) |
| 25    | tail     | C3A–C6A–C10A–O4A | 54.4 (2)   | −58.7 (4.3) |
| 26    | tail     | C3B–C6B–C10B–O4B | 61.0 (2)   | −58.7 (2.3) |
| 27    | tail     | C3C–C6C–C10C–O4C | 60.7 (2)   | −58.7 (2.0) |

Notes: (a) the colours highlight the torsions of most difference within each triplet: red 2–7, green 7–12 and blue >12. (b) Deviation from the ideal angle of 180°.

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and were given a ‘Low’ setting tolerance ‘Level of Geometric Similarity’. Where bifurcation was evident, individual PFF searches were performed for each partner pair and then for the two interactions together. The output of each search was recorded with a Positive result (a numerical and itemized list of known structures, with structure codes, that fell within the Low Level of Geometric Similarity), and a Negative result (included a corresponding numerical and itemized list of known structures containing the components of the search query, but where the geometric tolerances were not met). The reference codes of structures regarded as Positive and Negative hits under each PFF search result, and their total numbers and percentages, were compiled into Microsoft Excel spreadsheets. A spreadsheet of the results with matching Positive and Negative structure codes aligned (with the exception of search B1.2) was constructed (Table S2), and the numerical data summarized in graphical form (see Section 3.4.2).

2.3.2. Searches based on liberally defined structural motifs using the ConQuest search tool.

Loosely constrained structural motifs derived from those shown in Fig. S2 were established in the ConQuest search tool for propargylic donor interactions: CSM_A1, CSM_A2, CSM1_R1, CSM1-R2, CSM1_R3 and CSM1_R4; and acceptor interactions: CSM1_R5 and CSM1_R6 (Fig. S3). Relevant distance parameters, D1 (H/C1/C1/C1, Å) and D2 (D/C1/C1/C1, Å), were liberally defined as within the sum of the van der Waals radii plus 1.0 Å, and the angular measurements, ANG (D–H/C1/C1/C1, °), limited to within 60–180°. Where multiple contacts were recorded for a single compound, sometimes within the same category, these were included for

**Table 3**

| Strand/ Entry | Intra/ inter strand | D–A positions | D–H–A | D–H | H–A | D–A | Contact angle, θ |
|---------------|---------------------|---------------|-------|-----|-----|-----|-----------------|
| A             | intra tail–tail     | C13A–H13A–O6A | 0.95  | 2.34| 3.24 | 3.27 | 158.3           |
| 1             | inter head–tail     | C5A–H5A–C13A | 0.98  | 3.39| 3.46 | 3.46 | 86.1            |
| 2             | inter tail–head     | C17A–H17B–C6A | 0.98  | 2.98| 3.65 | 3.65 | 127.1           |

Symmetry codes: (i) x, y, z; (ii) x, y, z; (iii) x, y + 1, z.

and were given a ‘Low’ setting tolerance ‘Level of Geometric Similarity’. Where bifurcation was evident, individual PFF searches were performed for each partner pair and then for the two interactions together. The output of each search was recorded with a Positive result (a numerical and itemized list of known structures, with structure codes, that fell within the Low Level of Geometric Similarity), and a Negative result (included a corresponding numerical and itemized list of known structures containing the components of the search query, but where the geometric tolerances were not met). The reference codes of structures regarded as Positive and Negative hits under each PFF search result, and their total numbers and percentages, were compiled into Microsoft Excel spreadsheets. A spreadsheet of the results with matching Positive and Negative structure codes aligned (with the exception of search B1.2) was constructed (Table S2), and the numerical data summarized in graphical form (see Section 3.4.2).

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**Figure 3**

Inter- and intrastrand contacts between like molecules of strands A, B and C, as seen from directly above the mean planes of the A, B and C sheets, with unit cells indicated, as well as closeup views with labels and distance measurements included.
completeness. The values for D1, D2 and ANG for all matching contacts found in the CSD were recorded and the results displayed as scatterplots against ‘Identity Number’ in Fig. S3 and discussed more fully in Section 3.4.3.

3. Results and discussion

3.1. Molecules in the unit cell

The asymmetric unit comprises three independent molecules (represented as A-green, B-blue and C-red), each with the mannitol 2R,3R,4R,5R configuration [Fig. 1(b), randomly selected molecule A] and differing only in the conformation of the molecule. This establishes asymmetry in each molecule. Hence, in future, and for ease of reference, the terms ‘head’ and ‘tail’ sections will be used for each molecule, based on lower and higher crystallographic element numbers, respectively [Fig. 1(c)].

3.1.1. Conformations of molecules A–C. Based on torsion angles (Table 2), there are marginal differences in the conformation about the central mannitol core (Entries 1–3), with molecule A the most notable. Marginal differences are also observed in torsions associated with the orientation of the dioxolanyl groups relative to the core (Table 2, Entries 4–15), but most notably in molecule A and to the largest extent in the tail portion of the molecules. In contrast, puckering of the dioxolanyl group, as reflected in the C1/14—O3/10—C3/16—C6/10 torsion angles (Table 2, Entries 16–21), was most varied in the head section, and to the most significant extent (moderately) in molecule C; configurations in the tails of molecules A–C were highly consistent. The propargyloxy substituents potentially have three sources of conformational freedom. Marginal differences are observed in the torsions associated with their attachment to the mannitol core in both head and tail sections (Table 2, Entries 22–27), but most noticeably in molecule A. From this point, the orientation of the propargyl groups in comparison with the mannitol core are relatively conserved in the heads and tails of all three molecules (Table 2, Entries 28–33). However, significant differences are then observed in the orientations of the terminal acetylenic groups in the head and tail sections relative to the mannitol fragment (Table 2, Entries 34–39), with the most extreme difference appearing through atom O3 in the head of molecule A and atom O4 in the tail of molecule B.

3.2. Strand and sheet assemblies

3.2.1. Recognition of the like molecular strand construct. More detailed analysis reveals that, in the crystal, the three independent species (A-green, B-blue and C-red) align in strands, each with matching identical molecules A, B and C. Molecules in each strand engage through unique tail-to-tail

Figure 4
The unit cell of compound 1 viewed down the crystallographic b axis after rotating by 135° about the vertical axis, showing molecules A (green), B (blue) and C (red) with selected atom labels of close contacts as defined automatically within the limits of van der Waals radius —0.05 to 0.30 Å, within the crystal lattice, and an enlarged inset with details of the linear and orthogonal contacts involving C9B—H9B and C2C—H2CB with additional enforced distance measurements to C2C indicated. Note that the C9C—H9C—O2A contact was not detected under the conditions set for close contacts.
interactions. The differences in each case appear to arise because of subtle differences in the conformations of each molecule. Such individual strands all occur through C13—H13⋯O6 contacts and are represented and viewed along the a axis in Fig. 2(a) and along the c axis in Fig. 2(b). Thus, the contacts for molecules A (green) and B (blue) occur in a unidirectional sense along the b axis, with identical symmetry codes, namely (x + 1, y, z), while strands of molecules C (red) are oriented perpendicular, along the a axis [consider Figs. 2(a) and 2(b)], through a different symmetry code, (x, y − 1, z). As is also evident, particularly in Fig. 2(b) and the positions of atoms C5 and C9, the molecules in strands A and B are flipped relative to each other by approximately 180° about the length of the two strands. This feature permits near coincidence of the C13—H13⋯O6 alignments, with unidirectionality of the overall strands, while accommodating the steric demands of the remaining portions of the molecules.

3.2.2. Homogeneous molecular strands and sheets. 3.2.2.1. Intrastrand contacts between like molecules. Significant advances have been made towards estimating the H-atom positions of small organic molecules from X-ray crystallographic data (Jayatilaka & Dittrich, 2008; Capelli et al., 2014; Woitska et al., 2016). These have achieved results that are within the accuracy of neutron diffraction. However, a very limited number of examples have been described. As a consequence, contact data for short intra- and interstrand interactions between like molecules of each type have been summarized in Table 3 using parameters that have become accepted more widely as good indicators of strength and efficiency in the field for weak hydrogen bonds (Desiraju, 2005). The values include the accurately measured D⋯A distance (D, Å), the estimated D—H bond length using the previously utilized predicted position of the H atom for each type of weak acid species [CH (acetylenic) = 0.95 Å, CH (methylene at sp3 carbon) = 1.00 Å, CH2 (methylene) = 0.99 Å and CH3 (methyl) = 0.98 Å], without any additional normalization, and the resulting H⋯A distance (Å). Common to each of the strands are the aforementioned intrastrand tail-to-tail C13—H13⋯O6 contacts (Table 3; Entries 1, 4 and 12). All three achieve short D⋯A distances with near-linear D—H⋯A contact angles (A 158.3, B 164.7 and C 167.8°). Observed values are consistent with acetylenic groups with pKa (Me2SO) ~ 24.9 (Pedireddi & Desiraju, 1992). These intrastrand associations stand alone for molecule A, but are reinforced within the strands from molecule B by additional more distant C13—H13B⋯C14B, C13—H13B⋯C17B and C17B—H17D⋯H13B contacts (Table 3, Entries 5–7), and within those from molecule C by an equally distant head-to-head C4C—H4CB⋯C9C contact (Table 3, Entry 13) (see also Fig. 3). Those involving molecule B are exceptionally weak, as assessed by D⋯A distance measurements. They stem from additional engagement by the C13B—H13B group as a donor in a trifurcated contact with quaternary atom C14B and its neighbouring bonded methyl C17B and H17D atoms. The additional intrastrand contact involving molecules C is remarkable because it occurs between highly remote groups that ordinarily are weak donors and acceptors.

3.2.2.2. Interstrand contacts between like molecules. Interstrand contacts are also observed between like molecular strands (Table 3 and Fig. 3). These vary between parallel strands of molecules A, B and C with interstrand spacings, as measured by C13⋯C13′ distances of 10.300 (5), 10.300 (5) and 9.473 (4) Å, respectively, to create planar sheets of singular molecular type (Fig. 3). Donors in each case comprise normally weak dioxolanyl methyl groups, in which those between strands of A and B resemble each other, and those between strands C engage differently. For example, those from molecule A include a noticeably moderate C5A⋯C13A contact [D⋯A = 3.466 (4) Å] (Table 3, Entry 2) orthogonal to the aforementioned C13A—H13A⋯O6A interaction, while those from molecule B include a similar but specific C5B—H5BB⋯C12B contact [D⋯A = 3.612 (3) Å] (Table 3, Entry 8), neither of which are observed between the strands of molecule C. Similarly, molecule A participates in a weaker C17A—H17B⋯C8A contact with a propargylic acceptor (Table 3, Entry 3), while the equivalent donor group in molecule B, namely, C17B—H17E, engages in a bifurcated hydrogen-donor arrangement with the propargylic C7B⋯C8B bond (Table 3, Entries 9 and 10), neither of which are evident in the strands of molecule C. Molecule B is also involved in a separate propargylic H18E⋯C9B interaction (Table 3, Entry 11), which is absent in the strands of A, but is observed indirectly in those of molecule C (Fig. 3). Thus, molecule C shows a weak interstrand donor C4C—H4CC⋯C18C contact [D⋯A = 3.867 (4) Å], as well as the medium-strength interstrand C4C—H4CB⋯C9C contact [D⋯A = 3.456 (4) Å] (Table 3, Entries 14 and 13, respectively).

A consequence of these analyses is that, despite the orthogonal alignment of strands of molecules C relative to those of molecules A and B, the two-dimensional array of short contacts between like molecules in compound I is found to result in the formation of homogenous sheets of each molecular type.

3.2.3. Cross-strand/cross-sheet interactions. Separate molecular interactions occur between, rather than within, the sheets of molecules A–C. The nonconforming orientation of the C strand compared with the A and B strands, in particular, led us to examine even more closely this aspect of the supramolecular structure. In addition, the intermolecular interactions involving the propargylic C9—H9 acetylene donor functional groups in the head moieties were of interest. Contact data for these cross-strand/cross-sheet contacts (contacts between donors and acceptors from different molecular types A–C), almost all of which are ostensibly stronger C—H⋯O contacts, are summarized in Table 4. Contact angle (θ°), as well as distance measurements, are given for added depth of analyses. Values for intrastrand acetylenic C13—H13⋯O6 contacts are included for comparison (Table 4, Entries 1–3). As with the earlier analyses, it is acknowledged that the resulting data are derived from a single-crystal X-ray crystallographic study and not a comprehensive crystallographic database search. However, the observations and conclusions drawn from them are based on comparisons from well debated past literature.
Cross-strand acetylenic C9—H9 donor interactions occur from molecules A, B and C (Table 4, Entries 4–6). Superficially, those from molecules A (green) and B (blue) engage in unique finger-like intrusions, that are almost perpendicular to the axis of the parent strand, into separate strands of molecules C (red) [Fig. 2(b)], yet each one of the three contacts is different in detail. Readers will find Fig. 4 helpful in providing a pictorial view of the short contacts within the unit cell, as expressed in Table 4.

3.2.3.1. Cross-strand interactions from the standpoint of donor elements. Interstrand interactions are grouped in Table 4 according to notional donor acid strength, as defined by calculated D—H bond lengths, which are based on donor-atom electronegativity. This classification does not correlate directly with the understood mark of contact strength, namely, D •• A distance, even when contact angle (θ) is considered. The interactions in Table 4 are therefore discussed in this order, but within the context of three interaction types: singlet, pivot and couplet (see Fig. 5).

Molecules A (green) provide a modest cross-strand C9A—H9A acetylenic donor interaction with the tail dioxolanyl O6C atom in addition to the strong intrastrand, C13C—H13C donor contact with the same acceptor (Table 4, Entries 3 and 4). Because the acceptor O6C serves as a fulcrum in bringing together adjacent A and C molecules, the contact is called here a "pivot" interaction [Fig. 5(a)]. The short-to-medium C9A—H9A •• O6C contact distance [D = 3.376 (4) Å] is consistent with a slightly weaker acid than the acetylenic C13—H13 group (Pedireddi & Desiraju, 1992). Its contact angle (140.8°) (Table 4, Entry 4) is far from the near linear alignment of its partner (167.8°; Table 4, Entry 3) but within the range of other contacts from weak acids where interactions have been attributed to electrostatics (Desiraju, 1990; Pedireddi & Desiraju, 1992). However, in this pivot case, where both donors are of the same chemical type, the different D •• A distances is most likely a reflection of the different contact angles, with the linear contact being more dominant.

In a separate pivot interaction [Fig. 5(c)], molecules C (red) demonstrate a somewhat longer [D = 3.541 (2) Å] acetylenic donor contact (C9C—H9C •• O2A; Table 4, Entry 6), identified only by a directed measurement (therefore not visible in Fig. 4) with the head dioxolanyl group of an A molecule. The interaction is associated with another nonlinear contact angle (146.6°), but in this case made with a near linear contact (169.1°) with its pivot donor partner C4C—H4CB (Table 4, Entry 17). The donor in this portion of the pivot is derived from a dioxolanyl methyl group, which would normally be a much less acidic proton source than a terminal acetylenic group (compare the estimated D—H bond lengths of 0.98 versus 0.95 Å). The observed D •• A distances for the two interactions are indicative of the anticipated donor strengths, but closer in magnitude than one might expect. One explanation for their similarity is the acute angle of the first, which would diminish the donor effectiveness from its pKₐ and linearity of the latter, which would enhance effectiveness from its pKₐ for the methyl H atoms that are already the most acidic of those attached to sp² C atoms in compound I.

Contrasting these dioxolanyl contacts, molecules B (blue) participate in extremely short donor acetylenic C9B—H9B interactions [D = 3.121 (3) Å] with the head O3C propargylic ether O atom of molecules C (red) (see Fig. 4 and enlargement), with an accordingly near-linear contact angle (167.1°) (Table 4, Entry 5). The acetylenic C9B—H9B bond is also engaged in a secondary near-orthogonal contact with the nearby C2C—H2C bond (Fig. 4). This geometry is supported by the H9B—C9B •• C2C—H2CB torsion angle (ϕ = 83.8°; not recorded in Table 2) and small contact angles associated when the D—H group is considered C9B—H9B (107.4 and 112.1°; Table 4, Entries 7–8). However, the widely differing contact distance measurements (Table 4, Entries 7–10) for H •• A (D = 2.35–2.78 Å) and D •• A [D = 2.78–3.676 (3) Å] reflect a highly distorted orthogonal cluster. The close contact between participants H2CB •• C9B (2.78 Å) than H9B •• C2C (3.21 Å) and larger contact angle values with C2C—H2CB as the D—H group (145.5 and 150.3°) (Table 4, Entries 9–10) are most consistent with C2C—H2CB •• C9B being the main contact. This secondary interaction is suggestive of a bifurcated H2CB (Desiraju, 1991), which probably contributes to the extreme shortness of the C9B •• O3C distance.

These contacts, together, contribute to another type of cooperative set of contacts, called here a "couplet", that include in this example the non-acetylenic dioxolanyl methine C16B—H16B •• O1C contact [Table 4, Entry 16; Fig. 5(d)]. This is one of three couplet interactions [Figs. 5(b)–(d)] observed in the
crystals of compound 1 that, by definition, bring together two interstrand partners through two independent D⋯A contacts. In this example, the bifurcated H-atom donor from C2C—H2CB and its contact with the acetylenic C9B as an acceptor contribute to a ‘symmetrical’ (donor and acceptor in each molecular contributor) 11-membered ring of couplet atoms. Alternatively, the bifurcated H atom can be considered as contributing to a wider 15-membered ‘unsymmetrical’ couplet involving the C9B—H9B⋯O3C contact; in this situation, the two donor components participate from B molecules while the acceptors are located in C molecules in an unsymmetrical alliance. Couplets of either type can limit conformational flexibility and distort normal contact angles or, through their attractive nature, force contacts closer together. In the case of the methine C16B—H16B⋯O1C interaction, the D⋯A contact distance [D = 3.584 (3) Å] (Table 4, Entry 16) is

Figure 5
Major types of oxygen-acceptor-centred short interstrand contacts in the X-ray crystal structure of compound 1, with key atomic labels and bond angles, as recorded by Mercury (Version 2020.3.0; Macrae et al., 2020), for molecules A (green), B (blue) and C (red).
somewhat longer than for the only other methine contact, C6C—H6C···O1A (Entry 15), for which the contact angle is smaller. However, it is nearly identical to those of the pivot partners around O2A (Table 4, Entries 6 and 17), wherein contact angles are unequal. It is also very similar to those of methyl donor contacts C5B—H5B···O3A and C18A—H18B···O5C (Entries 18 and 19) with more linear contact angles. The medium-to-large D···A distance in the case of C16B—H16B···O1C is possibly the result of it being part of a reasonably large couplet of atoms, and its contact angle the result of confinement of the donor C16B—H16B bond as part of the tail dioxolanyl ring system in molecule B.

Three non-acetylenic donor types of C—H···O close contacts are recognisable within the distance range initially defined, and all are cross-strand (see Fig. 3). Those recorded as Entries 11–14 in Table 4 are considered in the first category because they involve similarly weakly acidic D···H participants (note the longer estimated D···H distances for Entries 9–14 compared with those for the acetylenic donor examples in Entries 1–8). They proceed from the methylene groups at atoms C7 and C11 in the head and tail propargyloxy substituents, respectively, but their interactions are in turn each different.

Molecules A and B make reciprocal head-group methylene contacts with the dioxolanyl O1 acceptor from the partner molecule. Notably, the donor from molecule B (Entry 12) makes a ‘singlet’ contact with O1A [Fig. 5(g)], that is, a contact without the involvement of any other partner. The singlet C7B—H7BA···O1B contact is closer [D = 3.261 (2) Å] and more linear (165.8°) than the C7A—H7AA···O1B contact from molecule A [Entry 11; D = 3.393 (2) Å, θ = 142.5°], which is part of another symmetrical seven-membered couplet [Fig. 5(c)] with the donor methyl C5B—H5BA···O3A interaction [Entry 18, D = 3.525 (3) Å, θ = 160.0°]. The smaller ring size of this tight couplet appears to impart a more acute angle to the C7A—H7AA···O1B contact and thereby must reduce the D···A distance. In contrast, only C11C—H11E participates as donor from the equivalent methylene group of molecule C, but the same donor makes contact with two quite different acceptors, namely, dioxolanyl O2B and C3B, with very different D···A distances. However, these acceptors reside at adjacent positions in the same molecule B (Table 3, Entries 13 and 14), and largely for this reason the contact is defined here as a ‘singlet’ interaction [Fig. 5(f)]. As expected, because the acceptor O2B has two frontier orbitals, each with lone pairs of electrons, contact with O2B is much shorter and more linear [Entry 13, D = 3.372 (3) Å, θ = 176.9°] with respect to the predicted C11C—H11E bond than it is with the adjacent methine C3B acceptor [Entry 14, D = 3.687 (4) Å, θ = 146.7°], with no free bonding electron pairs. The fact that atom H11E is bifurcated probably accounts for the slightly longer C11C···O2B contact compared with the C7B···O1A contact, but with a distance that is tempered by the near perfect alignment of the former.

The second type of non-acetylenic donor close contacts exhibit methine donor contributions from C6C—H6C and C16B—H16B, respectively (Table 4, Entries 15 and 16). Contacts occur with interstrand dioxolanyl oxygen partners, but with only moderate D···A distances (D) and contact bond angles (θ). Both C atoms are derived from the mannitol skeleton, the first bearing a propargyloxy substituent and the other an oxygen substituent that is part of the tail dioxolanyl group. It is possibly significant that none of molecules A—C exhibit close contacts involving donor C—H bonds from either of the symmetry-equivalent atoms C10 and C3, respectively, of these positions. However, it is worth recalling that C3B does participate in a contact with donor C11C—H11E (Table 4, Entry 14), but only as a weak acceptor, and then with limited efficiency. Donor C16B—H16B was also mentioned earlier as a close contact with O1C within the first couplet complex [Fig. 5(d)], with C9B—H9B···O3C. The remaining methine donor contact, C6C—H6C···O5A (Table 4, Entry 15), participates in an unsymmetrical nine-membered couplet with a tail–tail methyl donor contact, C18B—H18B···O5C [Table 4, Entry 19; Fig. 5(b)]. Perhaps because of its slightly different methine donor character, the C6C—H6C···O5A contact has a measurably shorter D···A distance [D = 3.457 (2) Å] than the C16B—H16B···O1C contact [D = 3.584 (3) Å] (Table 4, Entries 15 and 16). Equally, the difference in D···A contact distances might arise from the smaller contact angle for C6C—H6C···O5A brought about by constraints of its smaller ring couplet than those of the larger one involving C16B—H16B···O1C. Finally, the three remaining non-acetylenic donor contacts emanate from a C—H bond in one of the slightly more acidic, axial or equatorial geminal methyl groups attached to the dioxolanyl groups (Table 4, Entries 17–19). The three donors interact either head–head or tail–tail with a dioxolanyl O-atom acceptor and have comparable D···A distances (D) with near-linear contact angles (θ). All these contacts have been discussed above within the context of other interactions (Table 4, Entries 6, 15, and 16).

Between them, this complex array of contacts affords stability to the observed alternating layered sheets of A (green)–C (red)–B (blue) molecules (Fig. 6). The arrangement leaves no interdigitation of propargyl groups between layers of molecules of type A (green) and B (blue). However, there are alternative A···B reciprocal C—H···O contacts (Table 4, Entries 11–12 and 18), of which the head-to-head propargylic C7B—H7B···O1A contact and nonpropargylic C5B—H5BA···O3A contact are most important.

With this improved understanding of contacts from the perspective of C—H donors, a brief study was made of the geometry about the most important cross-strand contact acceptors in compound I, the relevant dioxolanyl and propargyloxy ether O atoms.

3.2.3.2. Cross-strand interactions from the standpoint of O-atom acceptors. Data derived from measurements of individual bond and contact angles associated with covalently bound O atoms and their close intermolecular donor C—H contacts are summarized in Table 5. This process was initiated on the questionable premise that acceptor interactions would take place through O-atom lone pairs of electrons (Taylor & Kennard, 1982, 1984; Steiner & Desiraju, 1998) and with the intention of providing better insight into the geometry at the acceptor sites.
The method used acknowledges that the O atoms in molecule I are all ethers and should have an electron-pair geometry that is approximately tetrahedral with coordinate angles of 109.5°. Accordingly, the sum of the triplet of bond and contact angles surrounding each relevant acceptor O atom has been calculated and the geometry arbitrarily assessed as ‘pyramidal’ (trigonal pyramidal) or ‘planar’, depending on whether the angle sum is less or more, respectively, than 344°, midway between the ideal for tetrahedral (328.5°) and planar (360°). In this study, close donor–acceptor (D···A) contacts are limited to those shorter than the sum of the van der Waals radii minus 0.01 Å. Under these conditions, atoms O2C, O3B, O4A–O4C and O5B showed no close contacts. In Table 5, the values of the D···A distance (D, Å) and contact angle (θ, °) of each observed C···H···O short contact are repeated from Table 4 and the contact types from Fig. 5 are added, all for reference purposes and as an aid to interpretation.

Surprisingly, only six of the 14 contacts with O atoms can be classified as pyramidal in their geometry. While all these are associated with dioxolanyl O atoms, not all the dioxolanyl classified as pyramidal in their geometry. While all these are.

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Table 4 and the contact types from Fig. 5 are added, all for reference purposes and as an aid to interpretation.

Surprisingly, only six of the 14 contacts with O atoms can be classified as pyramidal in their geometry. While all these are associated with dioxolanyl O atoms, not all the dioxolanyl O-atom contacts can be classified in this way. As partly discussed in the context of donors, in two of the six cases, dioxolanyl atoms O6C (tail) and O2A (head) each makes pivot contacts with two C···H donors (Table 4, Entries 3/4 and 6/17, respectively). This gives the interactions a degree of complexity, but with some hope of understanding differences in the geometry at the fulcrum, which is their O atom. In the first case [Table 5, Entries 3 and 4; Fig. 5(a)], two of the angular components used to evaluate the pyramidal or planar geometry about O6C are nearly identical, but the C15C—O6A···D angle differs markedly, i.e. 135.4 (1)° when D = C13C and 99.2 (1)° when D = C9A. The rendition of these contacts in Fig. 5(a) gives insight into the competition by donors C13C—H13C and C9A—H9A for access to O6C. It also gives an understanding as to how the closer more linear contact resulting from the former might have arisen through an overall planar geometry with O6C, with a splaying of the C15C—O6A···C13C angle, and a slightly weaker more apical contact at O6C through an acute angular interaction (probably electrostatic) by C9A—H9A. In the second pivot example [Table 5, Entries 9 and 10; Fig. 5(b)], a similar interplay appears to be involved, but the less acidic donor partner, C4C—H4CB, exerts a closer than expected near-linear contact with acceptor O2A at an angle sum [341.5 (2)°] that is close to being defined as that for a planar contact. As a result, the C1A—O2A···C4C and C3A—O2A···C9C component angles are increased and the C9C—H9C···O2A contact weakened concomitantly with a decrease in the observed contact angle to 146.6°.

Analyses of observed geometries around each of the O-atom acceptors in the three sets of couplet interactions reported in Table 5 (Entries 5–8 and 13–14) reveal that the observations are consistent with similar compromises in individual contributing angular components, contact distances and contact angles, but with additional consideration of the nature and size of the couplet. For example, in the symmetrical nine-membered couplet involving O5A and O5C [Fig. 5(b)], the unequal length of the carbon bridge between the donor and acceptor in molecule A (four atoms) and molecule C (five atoms) causes a severe enlargement of the internal C14A—O5A···C6C angle [143.1 (1)°] at the expense of the C16A—O5A···C6C angle [95.0 (1)°]. At the same time, the connectivity of the two D···A systems imposes the reverse distortion of the corresponding individual angles around O5C, with a

Figure 6
Close up of compound I, viewed along the a axis, with a slight offset showing differing interdigitation of C9—H9···O interactions between layers of independent molecules A (green), B (blue) and C (red), represented with non-H atoms as ellipsoids for clarity; key C—H donor partners are shown in darker colours.
compression of the internal C16−O5C···C18A angle [91.0 (1)°] at the expense of the C14C−O5C···C18A angle [137.0 (1)°]. The resulting shorter D···A contact for the former [D = 3.457 (2) Å] takes place through an acute D−H···A angle (135.6°) and planar though angularly distorted interaction with O5A. This result occurs despite the more linear (168.1°) contact of the normally more acidic methyl donor C18A−H18B with its couplet partner O5C. Analysis of the seven-membered couplet [Table 5, Entries 7 and 13; Fig. 5(c)] provides a similarly satisfying explanation for angular distortions around the O1B and O3A acceptors and indicates a more convincing dominance of one contact, the C7A−H7AA···O1B interaction, over the other.

The situation in the 11-membered couplet [Table 5, Entries 8 and 14; Fig. 5(d)] is more complex because of the participation of the orthogonal donor arrangement of the bifurcated H2C atom, but it is clear that equally explicable distortions of contributing angles around key acceptor components O1C, C9B and O3C do take place as a result of the couplet arrangement of the two partner components. Equally, tolerated distortions around the O2B and O1A acceptor O atoms in the two singlet cases [Table 5, Entries 11 and 12; Figs. 5(f) and 5(g)] are explicable for the simple reasons of neighbouring-atom participation and crystallographic dislocation of participants.

3.3. Crystal packing

A review of the crystallographic data to this point highlights a number of noteworthy features about compound I. The three independent molecules A−C that make up the unit cell differ subtly in conformation, but significantly at two of their ether sites. They each assemble into unique linear strands of like molecules, primarily through C13−H13···O6 contacts, but supported by intramolecular and intrashort interactions. Furthermore, the assemblies are unidirectional, with the strands of A and B aligned in close proximity, head-to-tail, along the crystallographic a axis and those of C aligned orthogonal along the b axis. Additional interstrand interactions between like molecules establish a two-dimensional sheet array of like parallel strands. However, a network of donor−acceptor contacts occur between strands/sheets of unlike molecular type.

3.3.1. Molecular strand and sheet planes. Initial examination of the crystal packing reveals a repeat layering of the three molecular types in the order A (green)−B (blue)−C (red), when viewed along the a and b axes (Fig. 7). Analysis of the mean planes of each molecule across three separate strands confirms their parallel arrangement, which is most convincing in Fig. 7(a). Such layering is consistent with the establishment of sheets (Section 3.2.2.2).

Further analysis of the mean planes of the A, B and C molecules in their respective strands across a span of five molecules in each strand reveals tilts of 6.28, 12.51 and 23.52°, respectively, from the mean planes of the sheets of each molecular type, which are themselves separated unequally by
A \cdot B = 4.934 \text{Å}, B \cdot C = 4.866 \text{Å} and C \cdot A = 5.012 \text{Å} (Fig. 8).

In Fig. 7, the C13—H13-bearing propargyl group in each molecule is highlighted by encircling the group. Collectively the orientations of the encircled groups reinforce their orthogonality in the A and B strands relative to those in the C strands. The intrusion of the equivalent C9—H9-bearing propargyl groups from molecules A and B into the strands of molecule C and reciprocal angular intrusion of the group from molecule C only into strands of molecule A is noticeable in Fig. 7(a), and accounts for the minor differences in inter-sheet spacings. This leaves very little interaction between molecules A and B, as is evident in Fig. 7(b) and as was discussed in Section 3.2.3.1. Minor void spaces are visible, especially in Fig. 7(b), but these are too small for any molecular inclusions.

3.4. CSD searches based on Mercury Crystal Packing Features and ConQuest search motifs involving donor and acceptor acetylenic contacts observed in compound 1.

3.4.1. Background. In the preceding diffraction studies of compound 1, intra- and intermolecular contacts were observed in which acetylenic components of the two propargyl groups participated in various situations as C—H donors and as C—H acceptors. Two principal searches of the Cambridge Structural Database (CSD; Groom et al., 2016) were carried out in order to ascertain the prevalence of these interactions and their scope in crystal engineering. These comprised firstly a Mercury-based study using highly constrained contact motifs derived from its Crystal Packing Feature (PFF) (Fig. S1) using measurements taken directly from compound 1 (Fig. S2). The second study utilized the ConQuest search tool and more loosely defined motifs (CSM) (Fig. S3) that, while artificial in their construct, were again based on general interpretations of the observed contacts (Fig. S2). The outcomes of these searches are discussed separately.

3.4.2. Analysis of Mercury Crystal Packing Feature (PFF) search results. As a general observation from the results summarized in Fig. 9 and Table S2, the propargylic group gave more positive matches when it participated as a donor through its terminal acetylenic proton than when the group served as a proton acceptor (Fig. 9). An analysis of findings from each contact type is described in detail in the supporting information, and summarized in the following sections.

3.4.2.1. Propargyl group as donor. There were considerable differences when the propargyl group served as a donor. Searches C and D were the more populous in terms of positive and negative results, while search B was extremely variable, especially with respect to negative results. Searches were dependent upon D \cdot A distances, with the observed shorter distances of stand-alone strand-forming contacts in group A being less common than equivalent interstrand contact distances or distances involving shared contacts with adjacent acceptor atoms. This dependence showed strong variation with the nature of the acceptor atom and with the number and extent of prescription, including Cyclicity, in the atoms/groups associated with the acceptor atom.

3.4.2.2. Propargyl group as acceptor. Despite many fewer positive results from motifs E–J than from motifs A–D, the number of negative results from searches remained in excess of 70 in cases E–J, and there was less scope than in the A–D cases for varying attached groups to either D or A atoms. Cases G1.1 and H1.1 provided situations with equivalent D and A types where minor differences in numbers of positive results (1 versus 3, respectively, perfectly counterbalanced by the differences in negative results, 75 versus 73) were observed. It was not possible to determine if these resulted intrinsically from very slightly higher D \cdot A contact distances, or ultimately by the significantly different D—H \cdot A bond angles brought about by intermolecular intrastrand (G1.1) compared with interstrand (H1.1) contacts (Fig. 3 and Table 4).
This situation was helped marginally when the E1.1, F1.1 and F2.1 interactions were considered as a whole (Fig S1 and Table 3). The E1.1 and F2.1 features showed a similarity not evident in F1.1; the bond to the distal C atom to which their donor methyl groups are attached is nearly unidirectional to the axis of the methyl C atom to acetylenic C atom trajectory, while in F1.1 it is at an acute angle (Fig. S1). Despite this observation, individual analyses showed that the more accurately measureable $D \cdot \cdot \cdot A$ distances increased in the order $F2.1 \leq E1.1 \ll F1.1$, which was not the same as the order of the H $\cdot \cdot \cdot A$ distances ($F2.1 \leq F1.1 \ll E1.1$) or the $D - H \cdot \cdot \cdot A$ angles ($E1.1 < F2.1 \ll F1.1$). On the other hand, for E1.1 there were no positive results but 71 negative results, and for F1.1 and F2.1, both recorded 76 results, with four and three, respectively, recorded as positive.

It was concluded from the lack of direct correlation between any of these trends, including intrastand and interstrand interactions, and the observed number of positive results, that the E1.1, F1.1 and F2.1 features are equally common to those in G, H and I, in the solid state. Again, the $D \cdot \cdot \cdot A$ distances encountered in the crystal structure of compound 1 must impose tight limitations that are not commonly met in structures within the CSD.

3.4.2.3. Analysis of structure codes for negative search results. Analysis of the breakdown of structure codes from each search (Table S2) showed relatively good coherence in the structure codes in the negative results for categories A1, A2 and C–I, but not for B1.1–B1.3. This outcome appears to mark a change from cyclic to acyclic O-atom acceptors. A similar lack of coherence was observed, albeit to a less dramatic extent because of fewer overall search results, for PFF J1.2–J1.4. Here it was noted that the donor H atom was part of a cyclic methylene group rather than from an exocyclic methyl group. Such factors were therefore important in interpreting the negative search results.

3.4.2.4. Analysis of structure codes for positive search results. As for positive results, there was a degree of coherence between structure codes within each of the search PFFs A1.1–A1.4, A2.1–A2.4, B1.1–B1.3 and C1.1–C1.4. The differences that were observed were readily attributable to variations in the attachments to the common acceptor atom in each set. In contrast, there was no overall coherence in the codes in the positive results between the first three categories, i.e. A1, A2 and B1 (Table S2). Initial thoughts of donor type or $D \cdot \cdot \cdot A$ distance as the cause were ruled out. Instead, a much more subtle feature appeared to be at play, namely, a different type of O-atom acceptor (Fig. S2), the influence of which was not as evident in the negative results. The similarities in positive result structure codes between A2, C and D results could then be explained by H $\cdot \cdot \cdot C$ interactions in PFF C and D that were strongly influenced by the presence of the corresponding dioxolanyl-derived O—CH$_2$ attachment to the formal quaternary C-atom acceptors.

3.4.3. Analysis of loosely constrained ConQuest structural motif (CSM) search results. Despite the predominance of positive propargylic donor over acceptor interactions in strand assemblies in the crystal structure of compound 1, the absolute sum of positive and negative donor interactions in each category from the study in Section 3.4.2 remained remarkably small. This prompted a more general search of the CSD for less constrained structural motifs (Fig. S3) that encompassed the main features of those already examined but focused on H $\cdot \cdot \cdot A$ (D1) and $D \cdot \cdot \cdot A$ (D2) contact distances, and $D - H \cdot \cdot \cdot A$ (ANG) angles.

3.4.3.1. CSD Index Numbers versus contact distances and angles. Simple scatterplots of the individual D1, D2 and ANG
values versus the CSD Index Numbers, with their respective search structure motifs (Fig. S3), revealed different cluster patterns in the distances, and to some degree contact angles, of each category, but no direct correlations, particularly between cases of multiple independent contacts within the one structure.

3.4.3.2 Contact distances and distance differences versus contact angles. Far more useful patterns emerged when scatterplots were constructed of D1 and D2 distances versus D—H···A (ANG) contact angles for the most populous donor acetylenic contacts to O (CSM1_R1) and C (CSM1_R4) acceptor atoms on the one hand, and acceptor acetylenic contacts at terminal C atoms (CSM1_R5) and C atoms adjacent to the terminal C atoms (CSM1_R6) by sp³ C—H donors on the other [Fig. 10(a)].

All searches gave noticeable differences between D1 and D2 that became larger with increasing contact angles [upper portions of each plot in Fig. 10(b)]. Initial observations were codified by additionally recording scatterplots of D2–D1 values against contact angles for each contact motif [lower portions of each plot in Fig. 10(b)]. These showed a nonlinear progression of larger D2–D1 values with increasing contact angle. However, calculated trend lines for each set of the D1 and D2 distance curves unmasked stark differences for each search category in the contributions of D1 and D2. For example, at the two extremes, the CSM1_R1 interactions involved a relatively constant D2 (D···A) distance and decreasing D1 (H···A) distances, while those of the CSM1_R4 and CSM1_R6 interactions showed the opposite, with relatively constant D1 and decreasing D2 distances. In CSM1_R5, the D2 (D···A) distances increased marginally, while the D1 (H···A) distances decreased noticeably, with increasing D—H···A angle, indicating that both parameters contributed. Neither absolute magnitudes of D1 and D2 in each search category, which fell in the order CSM1_R1 < CSM1_R4 < CSM1_R5 ≈ CSM1_R6, nor reported contact angles, which fell within four different ranges, could account for these observations. Instead, it was concluded that the type of acceptor atom (O versus C and terminal versus nonterminal acetylenic C) was probably responsible.

Despite these anomalies, when the scatterplots of the numerical difference (D2–D1) in contact distances versus contact angle in each category were plotted together, the correlation curves were virtually superposable [Fig. 10(c)]. Modelling studies revealed that very minor variations in the correlation curves were attributable to the different fixed C—H donor bond lengths (0.95–1.00 Å) embedded in each data set. Of the seven data points that could be regarded as outliers from these acknowledged trends, six were attributable to features in the CSD structures for just one compound, WUJWAC [(R)-1-[(4S,5R)-5-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]but-3-yn-1-ol] (Heinrich et al., 2020) (1 × CSM1_R1, 1 × CSM1_R4, 3 × CSM1_R5 and 1 × CSM1_R6), and one attributable to one other compound, EHAKAZ.
(a) *ConQuest* search motifs (CSMs) used to define searches of propargylic donor and acceptor interactions using loosely constrained distances (D1 and D2) and D—H···A angles (ANG). (b) Scatterplots of D1 (blue), D2 (green) and D2–D1 (black)(Å) values *versus* ANG (°) values for interactions in molecules satisfying criteria for *ConQuest* search motifs CSM1-R1, CSM1-R4, CSM1-R5 and CSM1-R6, including lines of best fit for the D1 and D2 results. (c) Overlay of the four scatterplots of D2–D1 values *versus* contact angle (ANG) from Fig. 10(b) (with changed marker shapes and colours), as well as related data points (in red) for relevant contacts in compound 1.
strength is best assessed in a continuum of van der Waals contacts and electrostatic interactions. The evidence supports the notion that contact –H⋅⋅⋅A distance (D, Å), with a considerable flexibility in the D—H⋅⋅⋅A contact angle and the geometry about the acceptor, at least when A is oxygen or carbon.

Two secondary studies of the Cambridge Structural Database (CSD) using Mercury Crystal Packing Features (PFF) and ConQuest structural motifs, based on features identified in the crystals of compound 1 involving the propargyl group, add further insight into the value of 1 as a model for the study of weak interactions in the solid state. They give mathematical credence to the close correlation that exists in these D—H⋅⋅⋅A systems between the difference in distance between D⋯A and H⋯A, and the D—H⋯A angle, but point to different contributions that the D⋯A and H⋯A parameters can have in this correlation, depending upon the particular structural motif involved.

Overall, the studies described here provide new insight into factors involved in weak acetylenic H⋅⋅⋅A interactions and might well prove useful in guiding the design of chemoselective applications of such functional groups, especially where these are propagated in or close to the solid state.

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3,4-Bis-O-propargyl-1,2:5,6-di-O-isopropylidene-D-mannitol: a study of multiple weak hydrogen bonds in the solid state

Adnan I. Mohammed, Mohan M. Bhadbhade and Roger W. Read

Computing details
Data collection: APEX3 (Bruker, 2016); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

(1R,2R)-1,2-Bis[(R)-2,2-dimethyl-1,3-dioxolan-4-yl]-1,2-bis(prop-2-yn-1-yloxy)ethane

Crystal data

\[
\begin{align*}
\text{C}_{18}\text{H}_{26}\text{O}_6 & \\
M_r &= 338.39 \\
\text{Triclinic, P1} & \\
a &= 9.4726 (4) \text{ Å} \\
b &= 10.3000 (5) \text{ Å} \\
c &= 15.3583 (7) \text{ Å} \\
\alpha &= 73.378 (2)^\circ \\
\beta &= 88.382 (2)^\circ \\
\gamma &= 86.400 (2)^\circ \\
V &= 1432.94 (11) \text{ Å}^3 \\
Z &= 3 \\
F(000) &= 546 \\
D_x &= 1.176 \text{ Mg m}^{-3} \\
\text{Mo K\(\alpha\) radiation, } & \\
\lambda &= 0.71073 \text{ Å} \\
\text{Cell parameters from 9994 reflections} & \\
\theta &= 2.6–30.4^\circ \\
\mu &= 0.09 \text{ mm}^{-1} \\
T &= 150 \text{ K} \\
\text{Block, colourless} & \\
V &= 0.24 \times 0.21 \times 0.19 \text{ mm}^3 \\
\end{align*}
\]

Data collection

Bruker APEXII CCD diffractometer
Graphite monochromator
\(\phi\) and \(\omega\) scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
\(T_{\min } = 0.679, T_{\max } = 0.746\)
25389 measured reflections

Refinement

Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.026\)
\(wR(F^2) = 0.065\)
\(S = 1.02\)
8343 reflections
661 parameters
3 restraints

Hydrogen site location: inferred from neighbour sites
H-atom parameters constrained
\(w = 1/[\sigma(F^2) + (0.032P)^2 + 0.2227P]\)
where \(P = (F^2 + 2F_c^2)/3\)
\((\Delta/\sigma)_{\text{max}} < 0.001\)
\(\Delta\rho_{\text{max}} = 0.21 \text{ e Å}^{-3}\)
\(\Delta\rho_{\text{min}} = -0.15 \text{ e Å}^{-3}\)
Absolute structure: Flack $x$ determined using
3228 quotients $|(I+)-(I-)|/(|(I+)+(I-)|)$ (Parsons et al., 2013)
Absolute structure parameter: 0.04 (17)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. A colourless block-like crystal of 1 with the dimensions $0.19 \times 0.21 \times 0.24$ mm, selected under a polarizing microscope (Leica M165Z), was picked up on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker kappa-II CCD diffractometer at 150 K using $\mu$S Incoatec Microfocus Source with Mo-Ka radiation ($\lambda = 0.710723$ Å). The single crystal, mounted on the goniometer using a cryo loop for intensity measurements, was coated with immersion oil type NVH and then quickly transferred to the cold nitrogen stream generated by an Oxford Cryostream 700 series. Symmetry-related absorption corrections using the program SADABS (Bruker, 2016) were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX3 software (Bruker, 2016). The structure was solved by program SHELXT (Sheldrick, 2015a) (with intrinsic phasing) and the full-matrix least-square refinements were carried out using SHELXL (Sheldrick, 2015b) through the OLEX2 (Dolomanov, 2009) software platform. Details of the experimental crystallographic data collected for compound 1 are summarized in Table 1. The non-hydrogen atoms were refined anisotropically. The H atoms were not located in the difference Fourier map. Instead, the H atoms were placed geometrically and constrained according to their environment using different AFIX commands available in SHELXL (Sheldrick, 2015b) operating via the OLEX2 (Dolomanov, 2009) platform.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)

|     | x          | y          | z          | $U_{iso}$/$U_{eq}$ |
|-----|------------|------------|------------|--------------------|
| O1A | 0.5767 (2) | 0.36428 (16) | 0.40439 (11) | 0.0489 (4)         |
| O2A | 0.54541 (15) | 0.41366 (14) | 0.25379 (10) | 0.0330 (3)         |
| O3A | 0.24531 (14) | 0.50233 (13) | 0.28189 (9)  | 0.0290 (3)         |
| O4A | 0.32743 (15) | 0.73829 (14) | 0.32764 (10) | 0.0317 (3)         |
| O5A | 0.15270 (14) | 0.92079 (13) | 0.17358 (10) | 0.0289 (3)         |
| O6A | −0.00610 (14) | 0.85925 (14) | 0.28710 (10) | 0.0335 (3)         |
| C1A | 0.6383 (2) | 0.3393 (2)  | 0.32429 (16) | 0.0368 (5)         |
| C2A | 0.5095 (2) | 0.4969 (2)  | 0.37928 (14) | 0.0332 (5)         |
| H2AA | 0.565949 | 0.561019 | 0.398912 | 0.040* |
| H2AB | 0.413939 | 0.496536 | 0.407191 | 0.040* |
| C3A | 0.5001 (2) | 0.5369 (2)  | 0.27551 (14) | 0.0279 (4)         |
| H3A | 0.568748 | 0.607920 | 0.248585 | 0.034* |
| C4A | 0.7862 (3) | 0.3876 (3)  | 0.3084 (3)  | 0.0639 (8)         |
| H4AA | 0.822356 | 0.377996 | 0.250032 | 0.096* |
| H4AB | 0.847564 | 0.333064 | 0.357378 | 0.096* |
| H4AC | 0.784989 | 0.483173 | 0.307554 | 0.096* |
| C5A | 0.6321 (3) | 0.1904 (2)  | 0.33391 (19) | 0.0485 (6)         |
| H5AA | 0.533783 | 0.164730 | 0.343942 | 0.073* |
| H5AB | 0.689372 | 0.138090 | 0.385720 | 0.073* |
| H5AC | 0.669065 | 0.171312 | 0.278332 | 0.073* |
| C6A | 0.3554 (2) | 0.58493 (18) | 0.23527 (13) | 0.0247 (4)         |
| H6A | 0.357882 | 0.582720 | 0.170576 | 0.030* |
| Atom | x     | y     | z     | U11  | U22  | U33  | U12  | U13  | U23  |
|------|-------|-------|-------|------|------|------|------|------|------|
| C7A  | 0.2188(2) | 0.3889(2) | 0.24967(15) | 0.0342(5) |
| H7AA | 0.141175  | 0.338975  | 0.286288  | 0.041*   |
| H7AB | 0.304508  | 0.326512  | 0.258799  | 0.041*   |
| C8A  | 0.1808(3) | 0.4275(2) | 0.15384(17) | 0.0414(6) |
| H8A  | 0.1549(3) | 0.4568(3) | 0.0760(2)  | 0.0646(8) |
| C9A  | 0.133910  | 0.480487  | 0.013034  | 0.078*    |
| C10A | 0.31561(19)| 0.73038(19)| 0.23687(13) | 0.0242(4) |
| H10A | 0.383700  | 0.792082  | 0.197112  | 0.029*    |
| C11A | 0.3807(2) | 0.8610(2) | 0.33579(19) | 0.0416(6) |
| C12A | 0.343471  | 0.878119  | 0.392624  | 0.050*    |
| C13A | 0.346433  | 0.937705  | 0.284276  | 0.050*    |
| C14A | 0.5352(2) | 0.8555(2) | 0.33670(16) | 0.0368(5) |
| C15A | 0.6594(3) | 0.8510(3) | 0.3393(2)  | 0.0530(7) |
| H13A | 0.759777  | 0.847379  | 0.341310  | 0.064*    |
| C16A | 0.1668(2) | 0.77518(19)| 0.20149(14) | 0.0261(4) |
| H16A | 0.149377  | 0.739783  | 0.148767  | 0.031*    |
| C17A | 0.0309(3) | 1.0948(2) | 0.22541(18) | 0.0429(6) |
| H17A | -0.058732 | 1.120802  | 0.251044  | 0.064*    |
| H17B | 0.053129  | 1.164970  | 0.169404  | 0.064*    |
| C18A | 0.0953(2) | 0.9680(3) | 0.13585(18) | 0.0456(6) |
| H18A | -0.100003 | 0.878701  | 0.125695  | 0.068*    |
| H18B | -0.072469 | 1.035035  | 0.078440  | 0.068*    |
| H18C | -0.186838 | 0.994524  | 0.158902  | 0.068*    |
| O1B  | 1.0876(2) | 1.16915(16)| 0.43913(11) | 0.0492(4) |
| O2B  | 1.05781(15)| 1.13024(14)| 0.58974(10) | 0.0332(3) |
| O3B  | 0.76846(14)| 1.04616(13)| 0.56368(9)  | 0.0283(3) |
| O4B  | 0.86447(14)| 0.79556(13)| 0.53706(9)  | 0.0279(3) |
| O5B  | 0.72215(14)| 0.62521(13)| 0.69482(10) | 0.0317(3) |
| O6B  | 0.49602(15)| 0.71009(15)| 0.66106(12) | 0.0405(4) |
| C1B  | 1.1431(3) | 1.1998(2) | 0.51572(16) | 0.0395(5) |
| C2B  | 1.0363(2) | 1.0364(2) | 0.46958(14) | 0.0324(5) |
| C3B  | 1.102525  | 0.969835  | 0.451963  | 0.039*    |
| C4B  | 0.942460  | 1.034333  | 0.443360  | 0.039*    |
| C5B  | 1.0256(2) | 1.0047(2) | 0.57313(14) | 0.0277(4) |
| H3B  | 1.099290  | 0.932365  | 0.601679  | 0.033*    |
| C4B  | 1.2967(3) | 1.1509(3) | 0.5300(3)  | 0.0691(9) |
| C5B  | 1.360375  | 1.053342  | 0.536337  | 0.104*    |
| C6B  | 1.330406  | 1.168030  | 0.585202  | 0.104*    |
| H4BC | 1.352965  | 1.199614  | 0.477656  | 0.104*    |
| C5B  | 1.1180(3) | 1.3501(2) | 0.50326(19) | 0.0525(7) |
| H5BA | 1.171484  | 1.400440  | 0.450053  | 0.079*    |
| H5BB | 1.149366  | 1.371919  | 0.557434  | 0.079*    |
| H5BC | 1.016911  | 1.375531  | 0.494201  | 0.079*    |
| Atom | X       | Y       | Z       | U11   | U22   | U33   | U12   | U13   | U23   |
|------|---------|---------|---------|-------|-------|-------|-------|-------|-------|
| C6B  | 0.8814  | 0.9648  | 0.6158  | 0.0237|
| H6B  | 0.8776  | 0.9784  | 0.6778  | 0.028  |
| C7B  | 0.7308  | 1.1699  | 0.5867  | 0.0337 |
| H7BA | 0.6700  | 1.2300  | 0.5384  | 0.040  |
| H7BB | 0.8177  | 1.2172  | 0.5892  | 0.040  |
| C8B  | 0.6558  | 1.1457  | 0.6739  | 0.0386 |
| C9B  | 0.5940  | 1.1288  | 0.7426  | 0.0641 |
| H9B  | 0.5436  | 1.1150  | 0.7986  | 0.077  |
| C10B | 0.8592  | 0.8106  | 0.6255  | 0.0234 |
| H10B | 0.9392  | 0.7601  | 0.6617  | 0.028  |
| C11B | 0.9412  | 0.6735  | 0.5322  | 0.0348 |
| H11C | 0.9332  | 0.6640  | 0.4702  | 0.042  |
| C11D | 0.8983  | 0.5946  | 0.5753  | 0.042  |
| C12B | 1.0903  | 0.6724  | 0.5537  | 0.040  |
| C13B | 1.2085  | 0.6769  | 0.5753  | 0.0593 |
| C14B | 1.3034  | 0.6804  | 0.5926  | 0.071  |
| C15B | 0.5864  | 0.8195  | 0.6233  | 0.0354 |
| C15C | 0.5466  | 0.9050  | 0.6338  | 0.042  |
| H15D | 0.6015  | 0.8337  | 0.5573  | 0.042  |
| C16B | 0.7218  | 0.7704  | 0.6751  | 0.0274 |
| H16B | 0.7176  | 0.7958  | 0.7333  | 0.033  |
| C17B | 0.5916  | 0.5305  | 0.5995  | 0.0465 |
| C17C | 0.4996  | 0.4969  | 0.5915  | 0.070  |
| H17D | 0.6640  | 0.4556  | 0.6105  | 0.070  |
| H17E | 0.6163  | 0.6015  | 0.5445  | 0.070  |
| C18B | 0.5279  | 0.4917  | 0.7648  | 0.0493 |
| H18D | 0.5341  | 0.5314  | 0.8153  | 0.074  |
| C18C | 0.5844  | 0.4054  | 0.7784  | 0.074  |
| H18F | 0.4289  | 0.4757  | 0.7564  | 0.074  |
| O1C  | 0.6116  | 0.7540  | 0.9030  | 0.044  |
| O2C  | 0.5219  | 0.7601  | 1.0385  | 0.0351 |
| O3C  | 0.4686  | 1.0526  | 0.9397  | 0.0297 |
| O4C  | 0.2292  | 1.0140  | 0.8458  | 0.0341 |
| O5C  | 0.0281  | 1.1753  | 0.9217  | 0.0333 |
| O6C  | 0.1349  | 1.3753  | 0.8790  | 0.0353 |
| C1C  | 0.6185  | 0.6827  | 0.9964  | 0.0382 |
| C2C  | 0.4691  | 0.8041  | 0.8844  | 0.0357 |
| H2CA | 0.4159  | 0.7406  | 0.8619  | 0.043  |
| H2CB | 0.4648  | 0.8940  | 0.8384  | 0.043  |
| C3C  | 0.4087  | 0.8150  | 0.9766  | 0.0285 |
| H3C  | 0.3261  | 0.7566  | 0.9943  | 0.034  |
| C4C  | 0.5704  | 0.5399  | 1.0145  | 0.0485 |
| H4CA | 0.4737  | 0.5435  | 0.9925  | 0.073  |
| H4CB | 0.5726  | 0.4947  | 1.0800  | 0.073  |
| H4CC | 0.6337  | 0.4890  | 0.9829  | 0.073  |
| C5C  | 0.7649  | 0.6880  | 1.0296  | 0.0662 |
| H5CA | 0.8315  | 0.6336  | 1.0024  | 0.099  |
### Atomic displacement parameters (Å²)

|       | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-------|------|------|------|------|------|------|
| O1A   | 0.0747 (12) | 0.0358 (9) | 0.0325 (9) | 0.0204 (8) | −0.0159 (8) | −0.0075 (7) |
| O2A   | 0.0375 (8) | 0.0324 (8) | 0.0288 (8) | 0.0122 (6) | −0.0072 (6) | −0.0106 (6) |
| O3A   | 0.0056 (8) | 0.0255 (7) | 0.00274 (8) | −0.0074 (6) | 0.0032 (6) | −0.0075 (6) |
| O4A   | 0.0343 (8) | 0.0333 (8) | 0.0321 (8) | −0.0004 (6) | −0.0042 (6) | −0.0150 (6) |
| O5A   | 0.0055 (7) | 0.0239 (7) | 0.0336 (8) | 0.0025 (5) | 0.0026 (6) | −0.0033 (6) |
| O6A   | 0.0228 (7) | 0.0356 (8) | 0.0536 (8) | 0.0326 (8) | 0.0039 (6) | 0.0045 (6) |
| O7A   | 0.0059 (5) | 0.0330 (11) | 0.00354 (12) | 0.0114 (9) | −0.0134 (10) | −0.0101 (10) |
| C1A   | 0.0425 (12) | 0.0278 (10) | 0.0281 (11) | 0.0067 (9) | −0.0107 (9) | −0.0071 (9) |
| C2A   | 0.0435 (12) | 0.0247 (10) | 0.0267 (11) | 0.0028 (8) | −0.0029 (9) | −0.0066 (8) |
| C3A   | 0.0572 (15) | 0.0520 (16) | 0.0371 (13) | 0.0508 (16) | 0.0146 (11) | −0.0137 (13) | −0.0126 (12) |
| C4A   | 0.0228 (10) | 0.0247 (10) | 0.0190 (10) | −0.0003 (8) | 0.0018 (8) | −0.0040 (8) |

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| Atom  | U1    | U2    | U3    | U4    | U5    | U6    |
|-------|-------|-------|-------|-------|-------|-------|
| C7A   | 0.0399(12) | 0.0274(11) | 0.0366(12) | -0.0057(9) | -0.0024(10) | -0.0101(9) |
| C8A   | 0.0444(13) | 0.0408(13) | 0.0435(15) | -0.0112(10) | -0.0040(11) | -0.0171(11) |
| C9A   | 0.075(2) | 0.083(2) | 0.0406(17) | -0.0277(17) | -0.0117(15) | -0.0193(15) |
| C10A  | 0.0230(10) | 0.0241(9) | 0.0248(10) | -0.0015(7) | 0.0016(8) | -0.0062(8) |
| C11A  | 0.0340(12) | 0.0390(12) | 0.0618(16) | 0.0053(9) | -0.0117(11) | -0.0309(12) |
| C12A  | 0.0390(13) | 0.0278(11) | 0.0447(14) | -0.0017(9) | -0.0056(10) | -0.0114(10) |
| C13A  | 0.0352(14) | 0.0353(13) | 0.082(2) | -0.0049(10) | -0.0050(13) | -0.0056(13) |
| C14A  | 0.0242(10) | 0.0312(10) | 0.0296(11) | 0.0043(8) | -0.0005(8) | -0.0053(9) |
| C15A  | 0.0257(10) | 0.0307(11) | 0.0403(13) | -0.0019(8) | 0.0013(9) | -0.0046(9) |
| C16A  | 0.0275(10) | 0.0238(10) | 0.0262(11) | -0.0016(8) | -0.0088(8) | -0.0055(8) |
| C17A  | 0.0479(14) | 0.0345(12) | 0.0462(14) | 0.0075(10) | 0.0031(11) | -0.0138(11) |
| C18A  | 0.0346(13) | 0.0530(15) | 0.0448(14) | 0.0010(10) | -0.0101(11) | -0.0069(12) |
| O1B   | 0.0390(13) | 0.0278(11) | 0.0447(14) | -0.0017(9) | -0.0056(10) | -0.0114(10) |
| O2B   | 0.0317(7) | 0.0284(7) | 0.0229(7) | 0.0074(6) | -0.0044(6) | -0.0058(6) |
| O3B   | 0.0317(7) | 0.0284(7) | 0.0229(7) | 0.0074(6) | -0.0044(6) | -0.0058(6) |
| O4B   | 0.0427(8) | 0.0345(8) | 0.0247(7) | 0.0049(6) | -0.0046(6) | -0.0074(6) |
| O5B   | 0.0390(7) | 0.0312(7) | 0.0296(11) | 0.0043(8) | -0.0005(8) | -0.0053(9) |
| O6B   | 0.0464(13) | 0.0377(12) | 0.0339(12) | -0.0015(8) | 0.0077(9) | -0.0070(10) |
| O1C   | 0.0346(13) | 0.0312(10) | 0.0296(11) | 0.0043(8) | -0.0005(8) | -0.0053(9) |
| O2C   | 0.0390(11) | 0.0353(10) | 0.0343(9) | 0.0033(8) | 0.0074(8) | -0.0155(8) |

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### Geometric parameters (Å, °)

| Bond/Distance | Length (Å) | Angle (°) |
|---------------|------------|-----------|
| O1A—C1A       | 1.429 (3)  |           |
| O1A—C2A       | 1.423 (3)  |           |
| O2A—C1A       | 1.424 (3)  |           |
| O2A—C3A       | 1.440 (2)  |           |
| O3A—C6A       | 1.430 (2)  |           |
| O3A—C7A       | 1.431 (2)  |           |
| O4A—C10A      | 1.427 (2)  |           |
| O4A—C11A      | 1.429 (2)  |           |
| O5A—C14A      | 1.429 (2)  |           |
| O5A—C16A      | 1.436 (2)  |           |
| O6A—C14A      | 1.422 (3)  |           |
| O6A—C15A      | 1.428 (2)  |           |
| C1A—C4A       | 1.506 (4)  |           |
| C1A—C5A       | 1.503 (3)  |           |
| C2A—H2AB      | 0.9900     |           |
| C2A—H2AB      | 0.9900     |           |
| C2A—C3A       | 1.532 (3)  |           |
| C3A—H3A       | 1.0000     |           |
| C3A—C6A       | 1.514 (3)  |           |
| C4A—H4AB      | 0.9800     |           |
| C4A—H4AC      | 0.9800     |           |
| C5A—H5AA      | 0.9800     |           |
| C5A—H5AB      | 0.9800     |           |
| C6A—H6A       | 1.0000     |           |
| C6A—C10A      | 1.529 (2)  |           |
| C7A—H7AA      | 0.9900     |           |
| C7A—H7AB      | 0.9900     |           |
| C7A—C8A       | 1.460 (3)  |           |
| C8A—C9A       | 1.176 (4)  |           |
| C9A—H9A       | 0.9500     |           |
| C10A—H10A     | 1.0000     |           |

### Non-bonded contacts

- C7A—H7BA 0.9900
- C7B—H7BB 0.9900
- C7B—C8B 1.462 (3)
- C8B—C9B 1.166 (3)
- C9B—H9B 0.9500
- C10B—H10B 1.0000
- C10B—C16B 1.520 (3)
- C11B—H11C 0.9900
- C11B—H11D 0.9900
- C12B—C13B 1.184 (4)
- C13B—H13B 0.9500
- C14B—C17B 1.502 (3)
- C14B—C18B 1.506 (3)
- C15B—H15C 0.9900
- C15B—H15D 0.9900
- C15B—C16B 1.510 (3)
- C16B—H16B 1.0000
- C17B—H17D 0.9800
- C17B—H17E 0.9800
- C17B—H17F 0.9800
- C18B—H18D 0.9800
- C18B—H18E 0.9800
- C18B—H18F 0.9800

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C10A—C16A 1.521 (3) O5C—C14C 1.432 (3)
C11A—H11A 0.9900 O5C—C16C 1.436 (2)
C11A—H11B 0.9900 O6C—C14C 1.425 (3)
C11A—C12A 1.461 (3) O6C—C15C 1.440 (3)
C12A—C13A 1.176 (3) C1C—C4C 1.513 (3)
C13A—H13A 0.9500 C1C—C5C 1.500 (4)
C14A—C17A 1.509 (3) C2C—H2CA 0.9900
C14A—C18A 1.510 (3) C2C—H2CB 0.9900
C15A—H15A 0.9900 C2C—C3C 1.544 (3)
C15A—H15B 0.9900 C3C—H3C 1.0000
C15A—C16A 1.541 (3) C3C—C6C 1.528 (3)
C16A—H16A 1.0000 C4C—H4CA 0.9800
C17A—H17A 0.9800 C4C—H4CB 0.9800
C17A—H17B 0.9800 C4C—H4CC 0.9800
C17A—H17C 0.9800 C5C—H5CA 0.9800
C18A—H18A 0.9800 C5C—H5CB 0.9800
C18A—H18B 0.9800 C5C—H5CC 0.9800
C18A—H18C 0.9800 C6C—H6C 1.0000
O1B—C1B 1.424 (3) C6C—C10C 1.518 (3)
C1A—O2A—C3A 106.52 (15) C8B—C7B—H7BB 109.1
C6A—O3A—C7A 115.53 (14) C8B—C8B—C7B 178.5 (3)
C2A—O1A—C1A 107.92 (17) C8B—C9B—H9B 180.0
| Bond and Angle | Value (°) | Bond and Angle | Value (°) |
|----------------|----------|----------------|----------|
| C10A—O4A—C11A | 115.33 (16) | O4B—C10B—C6B | 108.79 (15) |
| C14A—O5A—C16A | 108.14 (13) | O4B—C10B—H10B | 108.1 |
| C14A—O6A—C15A | 106.41 (15) | O4B—C10B—C16B | 111.48 (15) |
| O1A—C1A—C4A | 111.1 (2) | C6B—C10B—H10B | 108.1 |
| O1A—C1A—C5A | 107.81 (19) | C16B—C10B—C6B | 112.16 (15) |
| O2A—C1A—O1A | 103.83 (16) | C16B—C10B—H10B | 108.1 |
| O2A—C1A—C4A | 111.7 (2) | O4B—C11B—H11C | 109.2 |
| O2A—C1A—C5A | 108.97 (18) | O4B—C11B—H11D | 109.2 |
| C5A—C1A—C4A | 113.0 (2) | O4B—C11B—C12B | 112.20 (16) |
| O1A—C2A—H2AA | 110.7 | H11C—C11B—H11D | 107.9 |
| O1A—C2A—H2AB | 110.7 | C12B—C11B—H11C | 109.2 |
| O1A—C2A—C3A | 105.18 (16) | C12B—C11B—H11D | 109.2 |
| H2AA—C2A—H2AB | 108.8 | C13B—C12B—C11B | 175.3 (2) |
| C3A—C2A—H2AA | 110.7 | C12B—C13B—H13B | 180.0 |
| O2A—C3A—C2A | 103.38 (16) | O5B—C14B—C17B | 108.60 (16) |
| O2A—C3A—H3A | 109.3 | O5B—C14B—C18B | 109.72 (19) |
| C1A—C4A—C5A | 111.1 (2) | O5B—C14B—O5B | 105.49 (15) |
| O3A—C6A—C3A | 113.10 (16) | O6B—C14B—C17B | 111.8 (2) |
| O3A—C6A—H6A | 109.5 | O6B—C14B—C18B | 107.34 (17) |
| O3A—C6A—C10A | 111.46 (16) | C17B—C14B—C18B | 113.59 (19) |
| C3A—C6A—C10A | 111.46 (16) | C17B—C14B—C18B | 113.59 (19) |
| O4A—C10A—C6A | 108.87 (16) | C17B—C14B—C18B | 113.59 (19) |
| Bond                  | Angle  | Bond                  | Angle  |
|----------------------|--------|----------------------|--------|
| O4A—C10A—H10A       | 108.7  | C14C—O5C—C16C       | 109.83 (15) |
| O4A—C10A—C16A       | 110.70 (14) | C14C—O6C—C15C       | 106.49 (14) |
| C6A—C10A—H10A       | 108.7  | O1C—C1C—O2C         | 103.88 (17) |
| C16A—C10A—C6A       | 111.23 (15) | O1C—C1C—C4C         | 111.61 (19) |
| C16A—C10A—H10A      | 108.7  | O1C—C1C—C5C         | 109.0 (2) |
| O4A—C11A—H11A       | 109.2  | O2C—C1C—C4C         | 109.82 (18) |
| O4A—C11A—H11B       | 109.2  | O2C—C1C—C5C         | 108.56 (18) |
| O4A—C11A—C12A       | 112.26 (17) | C5C—C1C—C4C        | 113.5 (2) |
| H11A—C11A—H11B      | 107.9  | O1C—C2C—H2CA        | 110.9 |
| C12A—C11A—H11A      | 109.2  | O1C—C2C—C2CB        | 110.9 |
| C12A—C11A—H11B      | 109.2  | O1C—C2C—C3C         | 104.41 (18) |
| C13A—C12A—C11A      | 178.6 (3) | H2CA—C2C—H2CB       | 108.9 |
| C12A—C13A—H13A      | 180.0  | C3C—C2C—H2CA        | 110.9 |
| O5A—C14A—C17A       | 108.41 (16) | C3C—C2C—H2CB       | 110.9 |
| O5A—C14A—C18A       | 110.89 (17) | O2C—C3C—C2C        | 103.92 (16) |
| O6A—C14A—O5A        | 103.97 (15) | O2C—C3C—C6C        | 109.3 |
| O6A—C14A—C17A       | 108.75 (17) | O2C—C3C—C6C        | 108.41 (15) |
| O6A—C14A—C18A       | 111.37 (17) | C2C—C3C—H3C        | 109.3 |
| C17A—C14A—C18A      | 113.02 (19) | C6C—C3C—C2C    | 116.41 (17) |
| O6A—C15A—H15A       | 110.9  | C6C—C3C—H3C         | 109.3 |
| O6A—C15A—H15B       | 110.9  | C1C—C4C—H4CA        | 109.5 |
| O6A—C15A—C16A       | 104.47 (15) | C1C—C4C—H4CB       | 109.5 |
| H15A—C15A—H15B      | 108.9  | C1C—C4C—H4CC        | 109.5 |
| C16A—C15A—H15A      | 110.9  | H4CA—C4C—H4CB       | 109.5 |
| C16A—C15A—H15B      | 110.9  | H4CA—C4C—H4CC       | 109.5 |
| O5A—C16A—C10A       | 108.88 (15) | H4CB—C4C—H4CC      | 109.5 |
| O5A—C16A—C15A       | 103.72 (15) | C1C—C5C—H5CA       | 109.5 |
| O5A—C16A—H16A       | 109.9  | C1C—C5C—H5CB        | 109.5 |
| C10A—C16A—C15A      | 114.47 (17) | C1C—C5C—H5CC       | 109.5 |
| C10A—C16A—H16A      | 109.9  | H5CA—C5C—H5CB       | 109.5 |
| C15A—C16A—H16A      | 109.9  | H5CA—C5C—H5CC       | 109.5 |
| C14A—C17A—H17A      | 109.5  | H5CB—C5C—H5CC       | 109.5 |
| C14A—C17A—H17B      | 109.5  | O3C—C6C—C3C         | 111.51 (15) |
| C14A—C17A—H17C      | 109.5  | O3C—C6C—H6C         | 108.1 |
| H17A—C17A—H17B      | 109.5  | O3C—C6C—C10C        | 108.76 (15) |
| H17A—C17A—H17C      | 109.5  | C3C—C6C—H6C         | 108.1 |
| H17B—C17A—H17C      | 109.5  | C10C—C6C—C3C        | 112.04 (16) |
| C14A—C18A—H18A      | 109.5  | C10C—C6C—H6C        | 108.1 |
| C14A—C18A—H18B      | 109.5  | O3C—C7C—H7CA        | 109.1 |
| C14A—C18A—H18C      | 109.5  | O3C—C7C—H7CB        | 109.1 |
| H18A—C18A—H18B      | 109.5  | O3C—C7C—C8C         | 112.40 (19) |
| H18A—C18A—H18C      | 109.5  | H7CA—C7C—H7CB       | 107.9 |
| H18B—C18A—H18C      | 109.5  | C8C—C7C—H7CA        | 109.1 |
| C1B—O1B—C2B         | 107.75 (16) | C8C—C7C—H7CB       | 109.1 |
| C1B—O2B—C3B         | 106.77 (15) | C9C—C8C—C7C         | 179.2 (3) |
| C6B—O3B—C7B         | 114.46 (15) | C8C—C9C—H9C        | 180.0 |
| C11B—O4B—C10B       | 114.60 (16) | O4C—C10C—C6C        | 109.45 (15) |
| C14B—O5B—C16B       | 109.25 (15) | O4C—C10C—H10C      | 107.8 |
| Bond/Distance | Angle (°)  |
|--------------|-----------|
| C14B—O6B—C15B | 106.73 (14) |
| O1B—C1B—C4B | 111.2 (2) |
| O1B—C1B—C5B | 108.4 (2) |
| O2B—C1B—O1B | 104.31 (16) |
| O2B—C1B—C4B | 111.1 (2) |
| O2B—C1B—C5B | 108.03 (18) |
| C5B—C1B—C4B | 113.3 (2) |
| O1B—C2B—H2BA | 110.7 |
| O1B—C2B—H2BB | 110.7 |
| H2BA—C2B—H2BB | 108.8 |
| C3B—C2B—H2BA | 110.7 |
| C3B—C2B—H2BB | 110.7 |
| O2B—C3B—C2B | 103.53 (15) |
| O2B—C3B—H3B | 109.5 |
| O2B—C3B—C6B | 108.31 (15) |
| C2B—C3B—H3B | 109.5 |
| C6B—C3B—C2B | 116.29 (17) |
| C6B—C3B—H3B | 109.5 |
| C1B—C4B—H4BA | 109.5 |
| C1B—C4B—H4BB | 109.5 |
| C1B—C4B—H4BC | 109.5 |
| H4BA—C4B—H4BB | 109.5 |
| H4BA—C4B—H4BC | 109.5 |
| H4BB—C4B—H4BC | 109.5 |
| C1B—C5B—H5BA | 109.5 |
| C1B—C5B—H5BB | 109.5 |
| C1B—C5B—H5BC | 109.5 |
| H5BA—C5B—H5BB | 109.5 |
| H5BA—C5B—H5BC | 109.5 |
| O3B—C6B—C3B | 111.80 (15) |
| O3B—C6B—H6B | 108.4 |
| O3B—C6B—C10B | 108.72 (15) |
| C3B—C6B—H6B | 108.4 |
| C10B—C6B—C3B | 111.05 (15) |
| C10B—C6B—H6B | 108.4 |
| O3B—C7B—H7BA | 109.1 |
| O3B—C7B—H7BB | 109.1 |
| O3B—C7B—C8B | 112.38 (16) |
| H7BA—C7B—H7BB | 107.9 |
| C8B—C7B—H7BA | 109.1 |
| O1A—C2A—C3A—O2A | 8.0 (2) |
| O1A—C2A—C3A—C6A | 127.32 (18) |
| O2A—C3A—C6A—O3A | 71.97 (19) |
| O2A—C3A—C6A—C10A | −167.08 (14) |
| O3A—C6A—C10A—O4A | 69.86 (18) |
| O4C—C10C—C16C | 110.75 (16) |
| C6C—C10C—H10C | 107.8 |
| C6C—C10C—C16C | 112.93 (16) |
| O4C—C11C—H11F | 109.2 |
| O4C—C11C—C12C | 112.1 (2) |
| H11E—C11C—H11F | 107.9 |
| H11E—C11C—H11F | 109.2 |
| C3B—O2B—C1B—C5B | 151.4 (2) |
| C3B—C6B—C10B—O4B | −61.0 (2) |
| C3B—C6B—C10B—C16B | 175.18 (16) |
| C6B—O3B—C7B—C8B | −72.8 (2) |
| C6B—C10B—C16B—O5B | −170.17 (16) |
| Bond                           | Angle (deg) | Bond                           | Angle (deg) | Bond                           | Angle (deg) |
|--------------------------------|-------------|--------------------------------|-------------|--------------------------------|-------------|
| O3A—C6A—C10A—C16A             | 52.4 (2)    | C6B—C10B—C16B—C15B            | 73.8 (2)    |
| O4A—C10A—C16A—O5A            | 79.35 (18)  | C7B—O3B—C6B—C3B              | −88.03 (18) |
| O4A—C10A—C16A—C15A           | −36.2 (2)   | C7B—O3B—C6B—C10B             | 149.01 (15) |
| O6A—C15A—C16A—O5A            | −7.5 (2)    | C10B—O4B—C11B—C12B           | −63.2 (2)   |
| O6A—C15A—C16A—C10A           | 111.01 (18) | C11B—O4B—C10B—C6B            | 138.17 (16) |
| C1A—O1A—C2A—C3A              | 14.6 (2)    | C11B—O4B—C10B—C16B           | −97.64 (19) |
| C1A—O2A—C3A—C2A              | −27.7 (2)   | C14B—O5B—C16B—C10B           | −139.19 (17) |
| C1A—O2A—C3A—C6A              | −152.24 (16)| C14B—O5B—C16B—C15B           | −14.6 (2)   |
| C2A—O1A—C1A—O2A              | −31.9 (2)   | C14B—O6B—C15B—C16B           | −35.9 (2)   |
| C2A—O1A—C1A—C4A              | 88.2 (2)    | C15B—O6B—C14B—O5B            | 27.4 (2)    |
| C2A—O1A—C1A—C5A              | −147.4 (2)  | C15B—O6B—C14B—C17B           | −90.5 (2)   |
| C2A—C3A—C6A—O3A              | −44.4 (2)   | C15B—O6B—C14B—C18B           | 144.34 (19) |
| C2A—C3A—C6A—C10A             | 76.6 (2)    | C16B—O5B—C14B—O6B            | −7.0 (2)    |
| C3A—O2A—C1A—O1A              | 37.2 (2)    | C16B—O5B—C14B—C17B           | 112.93 (19) |
| C3A—O2A—C1A—C4A              | −82.5 (2)   | C16B—O5B—C14B—C18B           | −122.38 (18) |
| C3A—O2A—C1A—C5A              | 151.93 (18) | O1C—C2C—C3C—O2C              | 27.4 (2)    |
| C3A—C6A—C10A—O4A             | −54.44 (19) | O1C—C2C—C3C—C6C              | 115.03 (19) |
| C3A—C6A—C10A—C16A            | −176.68 (15)| O2C—C3C—C6C—O3C              | 73.42 (19)  |
| C6A—O3A—C7A—C8A              | −58.6 (2)   | O2C—C3C—C6C—C10C             | −164.40 (15) |
| C6A—C10A—C16A—O5A            | −159.48 (15)| O3C—C6C—C10C—O4C             | 63.06 (18)  |
| C6A—C10A—C16A—C15A           | 85.0 (2)    | O3C—C6C—C10C—C16C            | −60.82 (19) |
| C7A—O3A—C6A—C3A              | −88.7 (2)   | O4C—C10C—C16C—O5C            | 66.19 (19)  |
| C7A—O3A—C6A—C10A             | 148.04 (17) | O4C—C10C—C16C—C15C           | −49.8 (2)   |
| C10A—O4A—C11A—C12A           | −86.2 (2)   | O6C—C15C—C16C—O5C            | 29.57 (19)  |
| C11A—O4A—C10A—C6A            | 142.53 (16) | O6C—C15C—C16C—C10C           | 148.32 (17) |
| C11A—O4A—C10A—C16A           | −94.91 (19) | C1C—O1C—C2C—C3C              | 25.1 (2)    |
| C14A—O5A—C16A—C10A           | −137.44 (16)| C1C—O2C—C3C—C2C              | −17.9 (2)   |
| C14A—O5A—C16A—C15A           | −15.2 (2)   | C1C—O2C—C3C—C6C              | −142.36 (16) |
| C14A—O6A—C15A—C16A           | 27.5 (2)    | C2C—O1C—C1C—O2C              | −36.6 (2)   |
| C15A—O6A—C14A—O5A            | −37.32 (19) | C2C—O1C—C1C—C4C              | 81.6 (2)    |
| C15A—O6A—C14A—C17A           | −152.68 (17)| C2C—O1C—C1C—C5C              | −152.21 (18) |
| C15A—O6A—C14A—C18A           | 82.1 (2)    | C2C—C3C—C6C—O3C              | −43.2 (2)   |
| C16A—O5A—C14A—O6A            | 32.5 (2)    | C2C—C3C—C6C—C10C             | 79.0 (2)    |
| C16A—O5A—C14A—C17A           | 148.07 (17) | C3C—O2C—C1C—O1C              | 33.7 (2)    |
| O1B—C2B—C3B—O2B              | −87.3 (2)   | C3C—O2C—C1C—C4C              | −85.8 (2)   |
| O1B—C2B—C3B—C6B              | 61.2 (2)    | C3C—O2C—C1C—C5C              | 149.6 (2)   |
| O2B—C3B—C6B—O3B              | 74.95 (19)  | C3C—C6C—C10C—O4C             | −60.68 (19) |
| O2B—C3B—C6B—C10B             | −163.43 (16)| C6C—O3C—C7C—C8C              | −75.3 (2)   |
| O3B—C6B—C10B—O4B             | 62.37 (18)  | C6C—C10C—C16C—O5C            | −170.65 (15) |
| O3B—C6B—C10B—C16B            | −61.4 (2)   | C6C—C10C—C16C—C15C           | 73.3 (2)    |
| O4B—C10B—C16B—O5B            | 67.6 (2)    | C7C—O3C—C6C—C3C              | −88.57 (19) |
| O4B—C10B—C16B—C15B           | −48.5 (2)   | C7C—O3C—C6C—C10C             | 147.38 (16) |
| O6B—C15B—C16B—O5B            | 30.37 (19)  | C10C—O4C—C11C—C12C           | −88.7 (2)   |
| O6B—C15B—C16B—C10B           | 148.86 (16) | C11C—O4C—C10C—C6C            | 140.16 (17) |
| C1B—O1B—C2B—C3B              | 15.7 (2)    | C11C—O4C—C10C—C16C           | −94.69 (19) |
| C1B—O2B—C3B—C2B              | −25.8 (2)   | C14C—O5C—C16C—C10C           | −136.98 (16) |
| C1B—O2B—C3B—C6B              | −149.86 (18)| C14C—O5C—C16C—C15C           | −12.4 (2)   |
### Supporting Information

C2B—O1B—C1B—O2B  
C2B—O1B—C1B—C4B  
C2B—O1B—C1B—C5B  
C2B—C3B—C6B—O3B  
C2B—C3B—C6B—C10B  
C3B—O2B—C1B—O1B  
C3B—O2B—C1B—C4B  

Hydrogen-bond geometry (Å, °)

| D—H···A    | D—H  | H···A | D···A  | D—H···A |
|------------|-------|-------|--------|---------|
| C7A—H7AA···O1B  | 0.99  | 2.55  | 3.393 (3) | 143 |
| C9A—H9A···O6C  | 0.95  | 2.58  | 3.375 (3) | 141 |
| C13A—H13A···O6A  | 0.95  | 2.34  | 3.246 (3) | 158 |
| C18A—H18B···O5C  | 0.98  | 2.62  | 3.581 (3) | 168 |
| C5B—H5BA···O3A  | 0.98  | 2.59  | 3.525 (3) | 160 |
| C9B—H9B···O3C  | 0.95  | 2.19  | 3.121 (3) | 167 |
| C13B—H13B···O6B  | 0.95  | 2.21  | 3.138 (3) | 165 |
| C16B—H16B···O1C  | 1.00  | 2.69  | 3.584 (2) | 149 |
| C4C—H4CB···O2A  | 0.98  | 2.57  | 3.536 (3) | 169 |
| C6C—H6C···O5A  | 1.00  | 2.67  | 3.458 (2) | 136 |
| C9C—H9C···O2A  | 0.95  | 2.71  | 3.542 (3) | 147 |
| C11C—H11E···O2B  | 0.99  | 2.38  | 3.372 (3) | 177 |
| C13C—H13C···O6C  | 0.95  | 2.34  | 3.278 (3) | 168 |

Symmetry codes: (i) x−1, y−1, z; (ii) x, y−1, z−1; (iii) x+1, y, z; (iv) x, y, z−1; (v) x+1, y+1, z; (vi) x, y, z+1; (vii) x, y+1, z+1; (viii) x−1, y, z; (ix) x, y−1, z.