

Volume 78 (2022)

Supporting information for article:

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

Table of contents

- S1. Experimental
- S1.1. Synthesis
- S1. S1.2. Refinement
- **Table S1**Table S1. Hydrogen-bond geometry.

1.1. S1.3. Analyses of the Cambridge Structural Database (CSD)

1.1.1. S1.3.1. Searches of the CSD based on MERCURY Crystal Packing Features (PFF)

Figure S1 Figure S1. MERCURY Crystal Packing Features (PFF) used for searches of the CSD.

Figure S2 Figure S2. Structural features of 1 used to define PFF and CSM contact search motifs.

Table S2Table S2. Structure codes of positive and negative hits derived from MERCURY PFF searches.

S2. S1.3.2. Searches based on liberally defined structural motifs using the CONQUEST search tool

Figure S3 Figure S3. CONQUEST search motifs and CSD search results for Index Numbers *versus* D1, D2 (Å) and ANG (deg).

Figure 1 Figure S4. Molecular structures of compounds with outlier contacts in Figure 10(c).

S2. References

S1. Experimental

S1.1. Synthesis

The synthesis of 3,4-bis-*O*-propargyl-1,2:5,6-di-*O*-isopropylidene-D-mannitol **1** (IUPAC systematic name: (1R,2R)-1,2-bis((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-1,2-bis(prop-2-yn-1-yloxy)ethane has been reported (Mohammed, 2012) and the X-ray diffraction sample crystallized from EtOAc/*n*-hexane as colourless prisms, m.p. 50-52 °C.

S1.2. Refinement

A colourless block like crystal of 1 with dimensions of 0.19 X 0.21 X 0.24 mm³, selected under the 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 IµS Incoatec Microfocus Source with Mo-K α 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 fullmatrix least-square refinements were carried out using SHELXL (Sheldrick, 2015b) through the OLEX2 (Dolomanov, 2009) suite of software. Details of the experimental crystallographic data collected for compound 1 are summarized in Table 1. The non-hydrogen atoms were refined anisotropically but the hydrogen atoms were not located in the difference Fourier map. Instead, hydrogen atoms were geometrically placed and constrained according to their environment using different AFIX commands available in SHELXL (Sheldrick, 2015b) operating via the OLEX2 (Dolomanov, 2009) platform. The CCDC submission number is 2055328.

The geometric characteristics of hydrogen bonds are summarized in Table S1.

D—H···A	<i>D</i> —Н	Н…А	$D \cdots A$	D—H···A
$C7A$ — $H7AA$ ···· $O1B^{i}$	0.99	2.55	3.393 (3)	142.5
C9A—H9A····O6C ⁱⁱⁱ	0.95	2.58	3.375 (3)	140.8

Table S1	Hydrogen-bond	geometry (Å,	°)
----------	---------------	--------------	----

C13A—H13A····O6A ⁱⁱⁱ	0.95	2.34	3.246 (3)	158.2
C18A—H18B····O5C ^{iv}	0.98	2.62	3.581 (3)	168.1
C5B—H5BA····O3A ^v	0.98	2.59	3.525 (3)	160.0
С9В—Н9В…ОЗС	0.95	2.19	3.121 (3)	167.1
C13B—H13B…O6B ⁱⁱⁱ	0.95	2.21	3.138 (3)	164.7
C16B—H16B…O1C	1.00	2.69	3.584 (2)	149.1
C4C—H4CB····O2A ^{vi}	0.98	2.57	3.536 (3)	169.1
C6C—H6C····O5A ^{vi}	1.00	2.67	3.458 (2)	135.7
C9C—H9C····O2A ^{vii}	0.95	2.71	3.542 (3)	146.6
C11C—H11E····O2B ^{viii}	0.99	2.38	3.372 (3)	176.9
C13C—H13C····O6C ^{ix}	0.95	2.34	3.278 (3)	167.8

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*.

S1.3. Analyses of the Cambridge Structural Database (CSD)

S1.3.1. Searches of the CSD based on MERCURY Crystal Packing Features (PFF)

A total of thirty-three individual searches of the Cambridge Structural Database (CSD) for Crystal Packing Features (referred to here as PFFs) illustrated in Figure S1 were carried out on eleven unique sets of Donor D (A1, A2, B, C, D) and Acceptor A (E, F, G, H, I, J) propargylic contacts that were recognised within the crystal structure of compound 1 (Fig. S2). Search criteria specified consideration of Cyclicity 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 (Fig. 9, see Section 3.4.2).



Figure S1 MERCURY Crystal Packing Features (PFF) used for searches of the CSD.



NOTES: (1) **D**...**A** elements are as indicated after the search code; (2) **Fixed** search elements are indicated in bold; (3) Individually **varied** search elements are marked in parentheses.

Figure S2 Structural features of 1 used to define PFF and CSM contact search motifs.

Table S2Structure codes of positive and negative hits derived from MERCURY PFF searches (Table
contains two parts).

Search Positive hits Negative hits Total hits	A1.1	A1.2 1 -9 10	A1.3 1 -9 -3 10 3	A1.4 1 (34	A2.1 5 -3	A2.2 5 10 -: 15	A2.3 7 21 28	A2.4 4 -61 -1 65 1	B1.1 2 0 2	B1.2 2 5 -3 7 3	B1.3 6 5 330 -17 336 22	C1.1	C1.2 9 19 - 28	C1.3 4 24 - 28	C1.4 5 29 -1 34 2	D4 6 5 -3	D5 8 10 -2 18 2	D6 8 0 - 8	D7 8 1 20 -6 28 7	D8 10 1 56 -6 76 7	D9 .0 10 i6 -61 '6 70	E1 (5 -7: 5 7:	F1 0 1 -7 1 7	F2 4 12 -7 76 7	G1 3 -7 5 7	H1 1 3 5 -73 6 76	11 8 -7 5 7	12 2 -7 4 -7 6 7	13 2 4 -7 6 7	14 2 -2 74 -2 76 2	J1.2 0 7 -1 7 1	J1.3 0 11 -	J1.4 0 0 11 -11 11 11
% Positive % Negative		10 90	10 2 90 97	9 i 1 10		10	25 75 9	6.2 16. 13.8 83.	7 28 3 71	.6 .4 9	1.8 22.7 8.2 77.3	32	.1 14 .9 85	1.3 14 5.7 85	1.7 28 i.3 71	6 28 4 71	.6 28. .4 71.	6 28 4 71	.6 13 .4 86	.2 13 .8 86	.2 13. .8 86.1	2 (3 10	D 5 D 94	.3 3. .7 96.	9 1. 1 98.	3 3.9 7 96.1	9 2. 1 97.	6 2. 4 97.	6 2. 4 97.	.6 .4 10	0 10	0 30 1	0 0 .00 100
Pos RefCodes	JEWQIM	JENQIM	JENQIM		BEQGAI	BAGWAJ	HAMRUJ JEBQIT	HIHJEQ	GINGAM	EMAQEQ GINGAM	FEHNUD GOYZIG	BEQGAI HIHJEQ	BEQGAI	BEQGAI	BEQGAI EQAFEJ JENQIM	BAGWAJ BEQGAI HIHJEQ	BAGNAJ BEQGAI HIHJEQ	BAGWAJ BEQGAI HIHJEQ	BEQGAI	BEQGAI HIHJEQ	BEQGAI HIHJEQ	-	ehakaz eqafej	IHAFOO									
					KUPNER MUBBEQ	KUPNER MAYKAB	MUBBEQ		KELSOL	KEVWOZ KUPNEO	KELSOL	kupner Maykab Nepxuc	MAYKAB	KUPNUH MAYKAB	MAYKAB	KUPNUH MAYKAB NEPXUC	KUPNUH MAYKAB NEPXUC	KUPNUH MAYKAB NEPXUC	MAYKAB MOKBOF NEPXUC	MAYKAB MOKBOF NEPXUC	MAYKAB NOKBOF NEPXUC			OXULEA									
					WUJWAC	SOQBEG SUTWAI WUJWAC	WUJWAC	WUJWAC		WOWMIH XOXDOG	WALQUV	SOQBEG SUTWAI VOPHIU WUJWAC	SOQBIK	VOPHIU XIVCIO	SUTWAI WUJWAC	SOQBEG VOPHIU	SOQBEG VOPHIU	SOQBEG VOPHIU	QUYTIP SOQBEG VOPHIU XIVCIO YAHLUQ	QUYTIP SOQBEG VOPHIU XIVCIO YAHLUQ	QUYTIP SOQBEG VOPHIU XIVCIO YAHLUQ		SOQBIK SUTWAI				SAXLIP	SAXLIP	SAXLIP				
Neg RefCodes										330 Neg														YITFOY	ZEXMOE	YITFOY ZEXMIY ZEXMOE							
			ASUHOM		BOCFOO	BEQGAI	ACEHEW ACEROQ BEQGAI BOCFOO CIZFAV	BEQGAI	DIFOOZ		BOCFOO COSRAE DIFOOZ	BAGWAJ	BAGWAJ						BAGWAJ CEKGEH CIZFAV	BAGWAJ CEKGER CIZFAV	BAGWAJ CEKGEH CIZFAV	BAGWAJ BEQGAI CEKGEH CIZFAV	BAGNAJ BEQGAI CEKGEH CIZFAV	BAGNAJ BEQGAI CEKGEH CIZFAV	BAGWAJ BEQGAI CEKGEH CIZFAV	BAGNAJ BEQGAI CEKGEH CIZFAV	BAGWAJ BEQGAI CEKGEH CIZFAV	BAGWAJ BEQGAI CEKGEH CIZFAV	BAGWAJ BEQGAI CEKGEH CIZFAV	BAGWAJ BEQGAI CIZFAV			
	ehakaz Emakin	EHAKAZ EMAKIN	ehakaz emakin eqafaf eqafej	EHAKAZ	ehakaz Eqafaf	ehakaz eqafaf eqafej	EFAWAL EHAKAZ ENIJIV EQAFAF EQAFEJ ESUQOZ ETIROQ	EHAKAZ				ehakaz eqafaf eqafej	EHAKAZ EQAFAF EQAFEJ	EHAKAZ ENAKIN EQAFAF EQAFEJ	ehakaz emakin eqafaf	ehakaz Eqafaf Eqafej	ehakaz eqafaf eqafej	ehakaz eqafaf eqafej	EFEQIR EHAKAZ EMAKIN EQAFAF EQAFEJ	EFEQIR EHAKAZ EMAKIN EQAFAF EQAFEJ	EFEQIR EHAKAZ EMAKIN EQAFAF EQAFEJ	EFEQIR EHAKAZ EMAKIN EQAFAF EQAFEJ	EFEQIR EMAKIN EQAFAF	EFEQIR EHAKAZ EMAKIN EQAFAF EQAFEJ	EFEQIR EHAKAZ EMAKIN EQAFAF EQAFEJ	EFEQIR EHAKAZ EMAKIN EQAFAF EQAFEJ	EFEQIR EHAKAZ EMAKIN EQAFAF EQAFEJ	EFEQIR EHAKAZ EMAKIN EQAFAF EQAFEJ	EFEQIR EHAKAZ ENAKIN EQAFAF EQAFEJ	EQAFAF EQAFEJ	EHAKAZ	EHAKAZ	EHAKAZ
			FAKZID		HIHJEQ		FAKZID FONJID GUSYUQ HIHJEQ		GURDAB		GINGAM GURDAB HIRJEZ HIRJEZ01		нінјео	HIRJEZ HIRJEZO	1				HALSUJ HIRJEZ HIRJEZO1 HITKIG	HALSUJ HIRJEZ HIRJEZ01 HIRKIG	HALSUJ HIRJEZ HIRJEZO1 HITKIG	HALSUJ HIHJEQ HIRJEZ HIRJEZ01 HITKIG	HALSUJ HIHJEQ HIRJEZ HIRJEZOI HITKIG	HALSUJ HIHJEQ HIRJEZ HIRJEZ01 HITKIG	HALSUJ HIHJEQ HIRJEZ HIRJEZO1 HITKIG	HALSUJ HIHJEQ HIRJEZ HIRJEZO1 HITKIG	HALSUJ HIHJEQ HIRJEZ HIRJEZO1 HITKIG	HALSUJ HIHJEQ HIRJEZ HIRJEZ01 HITKIG	HALSUJ HIHJEQ HIRJEZ HIRJEZ01 HITKIG	HIHJEQ HIRJEZ HIRJEZ01	FAKZID	FAKZID	FAKZID
	IHAFOO	IHAFOO	IHAFOO IYEYES	IHAFOO	IHAFOO	IHAFOO	HUVGIP HUVGOV HUVGUB IHAFOO JEVVEO	IHAFOO				IHAFOO	IHAFOO	IGAZOF IHAFOO	IHAFOO	IHAFOO	IHAFOO	IHAFOO	HURLEN IGAZOF IHAFOO JUBTOS	HURLEN IGAZOF IHAFOO JUBTOS	HURLEN IGAZOF IHAFOO JUBTOS	HURLEN IGAZOF IHAFOO	HURLEN IGAZOF IHAFOO JUBTOS	HURLEN IGAZOF JUBTOS	HURLEN IGAZOF IHAFOO JUBTOS	HURLEN IGAZOF IHAFOO JUBTOS	HURLEN IGAZOF IHAFOO JUBTOS	HURLEN IGAZOF IHAFOO JUBTOS	HURLEN IGAZOF IHAFOO JUBTOS	IGAZOF	IHAFOO	IHAFOO	IHAFOO
	KIJDUD KUPNER KUPNUH	KIJDUD KUPNER KUPNUH	KEWYIX KIJDUD KUPNER KUPNUH KUWZOS LIHHIV	KIJDUD		KIJDUD KUPNUH LENHOE	KOVQAP KUPNER	KUPNER				KIJDUD KUPNUH LENHOE	KIJDUD KUPNER KUPNUH LENHOE	KUPNER	KIJDUD KUPNER KUPNUH	KIJDUD KUPNER LENHOE	KIJDUD KUPNER LENHOE	KIJDUD KUPNER LENHOE	KELSOL KIJDUD KUPNER KUPNUH LENHOE	KELSOL KIJDUD KUPNER KUPNUH LENHOE	KELSOL KIJDUD KUPNER KUPNUH LENHOE	KELSOL KIJDUD LENHOE	KELSOL KIJDUD KUPNER KUPNUH LENHOE	KELSOL	KUPNER KUPNUH LIHHIV	KUPNER KUPNUH LIBHIV	KUPNER KUPNUH LIHHIV						

Search	A1.1	A1.2	A1.3	A1.4	A2.1	A2.2	A2.3	A2.4	B1.1	B1.2	B1.3	C1.1	C1.2	C1.3	C1.4	D4	D5	D6	D7	D8	D9	E1	F1	F2	G1	H1	11	- 6
Positive hits Negative hits		-9	-9	-34	-5 -	20 ·	-21 ·	4 . 61 -10	0	-5	-330 -1	7 -	9 19 ·	-24 -	5 29 -1	ь 15 -	-20 ·	-20 -	8 20 -	10 66 ·	10 1 -66 -6	5 -71	1 -	4 72 -7	3 '3 -7	1 5 -7	3	-74
Total hits		10	10	35	5	25	28	65 13	2	7	336 2	2	28	28 LUYLOI	34 2	21	28	28	28 LUYLOI	76 LUYLOI	76 7 LUYLOI	5 71 LUYLOI	1 LUYLOI	76 7 LUYLOI	6 7	6 7	16 LUYLOI	76
					MAYKAB		MAYKAB	MAYKAB														MAYKAB	MAYKAB	MAYKAB	MAYKAB	MAYKAB	MAYKAB	. 8
														MOKBOF					MILLEY	MILLEY	MILLEY	MILLEY MOKBOF	MOKBOF	MOKBOF	MOKBOF	MILLEY MOKBOF	MILLEY MOKBOF	
					MERVIC	MUMQER	MUMQER	NERVIC				MUMQER	MUMQER	NERVIC		MUMQER	MUMQER	MUMQER	NUMQER	MUMQER	MUMQER	MUMQER	MUMQER	NUMQER	NUNGER	MUNQER	MUMQER	
			NEQSEJ		ALL NOC	ALLAGE	nut not	HEL NOC					Har Aoc	MELAUC								Mar Noc	nut not	HELAUC	Mar Abe	ALLAGE	ALL NOC	
														NICQEY					NICQEY									
			NODBEP																									
			NUPPUL																									
			OBUOAE						NUPVAX		NUPVAX																	
							OCACIG																					
	ojajoa	AOLALO	ADLALO				OCACIGO	1																				
											OLAVED								ORIDAW	ORIDAW	ORIDAN	ORIDAN	ORTDAW	ORIDAW	ORIDAM	OBIDAW	ORIDAN	
			OXOZAD			OXOZAD						OXOZAD	OXOZAD			OXOZAD	OXOZAD	OXOZAD	OXOZAD	OXOZAD	OXOZAD	OXOZAD	OXOZAD	OXOZAD	OXOZAD	OXOZAD	OXOZAD) (
			OXULEA PAHJEO																OXULEA	OXULEA	OXULEA	OXULEA	OXULEA		OXULEA	OXULEA	OXULEA	. 0
							PALMEX																					
									PEQKON										PIHPOO) 1								
							PRYURD1	0			PIJTEJ								PIJTEJ	1								
			QANTED				QAMTED																					
							QIPHII												01MG00	01MC00	01MG00	01NG00	019600	01M000	019000	018000	01MG00	
					OULUG		OULUG							QOYSED					QOYSED									
			QUMZEF				QUMZEF																					
														QUYTEL QUYTIP					QUYTEL	QUYTEL	QUYTEL	QUYTEL QUYTIP	QUYTEL QUYTIP	QUYTEL QUYTIP	QUYTEL QUYTIP	QUYTEL QUYTIP	QUYTEL QUYTIP	
							REGHUG				PTPNIIC								REGHUG	- 3								
							RIWNEQ				Rindo																	
					RODFIB		RODFIB												RODFUN									
					D.0. 717.12	DOTITY	ROHHII					DO BUTY	DO TUTY		DO TITY	DO THEY	0.000	DO THEY	DO THEY	DO 11/1	DO TITY	DO TUTY	DO TUTY	DO THEY		DOTIN	DO 7174	
					ROJVOE	ROJVOE	ROJVOE					ROJVOE	ROJVOE		ROJVOE	ROJVOE	ROJVOE	ROJVOE	ROJVOE	ROJVOE	ROJVOE	ROJVOE	ROJVOE	ROJVOE	ROJVOE	ROJVOE	ROJVOE	: 7
							SASFID												RUJZIH SASFID	. 5								
							SAXLIP							SAXLIP					SAXLIP									
													SOQBEG						SESDAX	SESDAX	SESDAX	SOQBEG	SOQBEG	SOQBEG	SOQBEG	SOQBEG	SOQBEG	; 5
					500800	SOQBIK	500800	SOOBOO				SOQBIK	SOOBOO		SOQBIK	SOQBIK	SOQBIK	SOQBIK	SOQBIK	SOQBIK	SOQBIK	SOQBIK	500800	SOQBIK	SOQBIK	SOQBIK	SOQBIK	: 5
																			SORKUI									
	SUTWAI	SUTWAI	SUTWAI	SUTWAI	SUTWAI		SOTPAU SUTWAI	SUTWAI					SUTWAI	SUTWAI		SUTWAI	SUTWAI	SUTWAI	SUTWAI	SUTWAI	SUTWAI			SUTWAI	SUTWAI	SUTWAI	SUTWAI	
			TAXTOD																TAQHIF									
							TEHVAE																					
														TIKKUW TOWJUM					TIKKUW TOWJUM	TIKKUW TONJUM	TIKKUW TOWJUM	TIKKUW TOWJUM	TIKKUW TOWJUM	TIKKUW TOWJUM	TIKKUW	TIKKUW	TIKKUW TOWJUM	1
			UGEBUD																		1713 6700							
																			UVASLU	UVASLU	UVASIU	UVASIU	UVASLU	UVASIU	UVASIU	UVASIU	UVASIU	r t
							UXAYEY												UVASOA	UVASOA	UVASOA	UVASOA	UVASOA	UVASOA	AORAVU	UVASOA	UVASOA	. t
														UXOGAQ					UXOGAQ	<i>c</i> . 1								
							VALVOW												VECDUF	. ,								
			VIJKOP			VOPHIU	VIJKOP						VOPHIU									VOPHIU	VOPHIU	VOPHIU	VOPHIU	VOPHIU	VOPHIU	
					VOXQEG	VOXQEG	VOXQEG					VOXQEG	VOXQEG		VOXQEG	VOXQEG	VOXQEG	VOXQEG	VOXQEG	VOXQEG	VOXQEG	VOXQEG	VOXQEG	VOXQEG	VOXQEG	VOXQEG	VOXQEG	. 1
					VUHRUI		VUBRUI				VUBROI																	
									WALQUV										WERPOR	WER POR	NERPOR	WERPOR	WERPOR	WERPOR	WERPOR	WERPOR	WERPOR	
																			WERPUH									
							WIYXOU												WIYXOU									
							WOYWOZ						WILTWAC	WILTWAC		MILTNAC	WILTWAC	WILTWAC	WILTWAC	WILTWAC	NILTNAC		WILTWAC	WILTWAC	WILTHAC	NULTWAC	WILTWAC	
							WUSQUY																					
			XESSIX XIVCIO		XIVCIO	XIVCIO	XIVCIO	XIVCIO				XIVCIO			XIVCIO	XIVCIO	XIVCIO	XIVCIO				XIVCIO	XIVCIO	XIVCIO	XIVCIO	XIVCIO	XIVCIO	
					VOCUT	VOCUTE	VACULT	V0.7111			XOCTEP	VOCUTI	VOCULT	X0.51177	WOGUTT	VOCUTE	VOCUTI	VOCULT	VACULT	VOCULI	W0071177	VOCULT	VOCUTE	VOCUTI	2000000	VOCUTI	VOCUTE	
					KOGHIL	AUGHIL	AUGHIL	AUGHIL			AUGHIL	AOGHIL	XUGHIL	YAHLUQ	XUGHIL	XUGHIL	AUGHIL	AUGHIL	AUGHIL	AUGHIL	XUGHIL	YAHLUQ	YAHLUQ	YAHLUQ	YAHLUQ	YAHLUQ	XOGHIL	
					YIBMEE	YEBSIJ	YEBSIJ YIBMEE					YEBSIJ	YEBSIJ			YEBSIJ	YEBSIJ	YEBSIJ	YEBSIJ	YEBSIJ	YEBSIJ	YEBSIJ	YEBSIJ	YEBSIJ	YEBSIJ	YEBSIJ	YEBSIJ	3
					YIBMEEÖ	1	YIBMEE 0	1														1				[
	YITFOY	YITFOY	YITFOY								AIRFOA			YITFOY	YITFOY				YITFOY	YITFOY	YITFOY	YITFOY	YITFOY		YITFOY		YITFOY	
						YITWIM						YITWUW	YITWIM	YITWUW		YITNUM	YITWIN	YITWUW	YITWUW	YITWIN	YITNUM	YITNUN	YITWUM	YITWUW	YITWUM	YITWUM	YITWIN	
						//					YOCKEJ						//											
														ZEXMIY					ZEXMIY ZEXMOE	ZEXMIY ZEXMOE	ZEXMIY ZEXMOE	ZEXMIY	ZEXMIY	ZEXMIY ZEXMOE	ZEXMIY		ZEXMIY ZEXMOE	: 1
L									1					ZODCED					ZODCED	2								

S1.3.2. Searches based on liberally defined structural motifs using the CONQUEST search tool

Loosely constrained structural motifs derived from those shown in Figure S2 were established in the CONQUESTTM search tool for propargylic Donor interactions: CSM_A1, CSM_A2, CSM1_R1, CSM1-R2, CSM1_R3, CSM1_R4, and Acceptor interactions: CSM1_R5 and CSM1_R6 (Fig. S3). Relevant distance parameters, D1 (\mathbf{H} ...A, Å) and D2 (\mathbf{D} ...A, Å), were liberally defined as within the sum of van der Waals radii + 1.0 Å, and the angular measurements, ANG (D–H...A, deg), limited to within 60–180 degrees. Where multiple contacts were recorded for a single compound, sometimes within the same category, these were included for completeness. The values for D1, D2, and ANG for all matching contacts found in the CSD were recorded and the results displayed as scatter plots against Identity Number in Figure S3 and discussed more fully in Section 3.4.3.



Figure S3 CONQUEST search motifs (right) and CSD search results showing scatter plots of Index Number versus D1 (blue) and D2 (green) (Å) (left) and ANG (orange) (deg) (middle) values.



Figure S4 Molecular structures of compounds with outlier contacts in Figure 10(*c*).

S2. References

Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Crystallogr.* **42**, 339–341.

Mohammed, A. I., Abboud, Z. H. & Alghanimi, A. H. O. (2012). *Tetrahedron Lett.* **53**, 5081–5083.

Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8. https://doi.org/10.1107/S2053273314026370

Sheldrick, G. M. (2015b). Acta Cryst. C71, 3-8. https://doi.org/10.1107/S2053229614024218