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The Synthesis and Structure of Substituted Dimenthyl Malonate Derivatives

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ABSTRACT A series of substituted dimenthyl malonate derivatives were efficiently synthesized from dimenthyl malonate using a deprotonation and alkylation strategy. The elucidation of the structure of these derivatives were determined by a combination of X-ray crystallography, NMR and IR spectroscopy.

KEYWORDS alkylation, deprotonation, malonate, structure determination and symmetry

The synthesis of substituted 1,3-dicarbonyl derivatives is very well documented [1]. Reports into the structural nature of these derivatives are less common [2]. The majority of these reports have dealt with substituted malonic acid derivatives [3], whereas some attention has been focused on related keto- [4] and aldehyde derivatives [5]. By comparison, little is known about malonic ester derivatives [6]. However, through single crystal x-ray structure determination, substituted malonic acids [7] have been shown to exist in an intramolecular or intermolecular hydrogen bonded arrangement; where both carbonyl groups are positioned in an *anti*-relationship **A**, rather than a *syn*-relationship **S** (Figure 1). This *anti*-conformer arrangement is also evident in their related malonate salts [8]. However, in the absence of intramolecular hydrogen bonding and internal metal co-ordination; keto- [9] and aldehyde [10] derivatives have been shown to adopt a wide range of conformers (ranging from *anti*-alignment through to perpendicular and *syn*-alignment of both carbonyl groups) within the crystal phase, whereas related substituted malonate esters have been shown to preferentially adopt a *syn*-alignment [11].

We previously investigated the use of 1,3-dicarbonyl containing molecules as achiral proton donor in the enantio- [12] and regioselective protonation [13] of prostereogenic enolates. However, reports into the preferred conformation of these chiral carbon-based acids are limited [14]. In an attempt to increase this understanding, we chose to synthesize a series of related dimenthyl malonate derivatives and examine their conformational preferences using single crystal x-ray crystallography.

We first synthesized the symmetrical dimenthyl malonate **2** and investigated its structural properties. We chose to use enantiomerically pure

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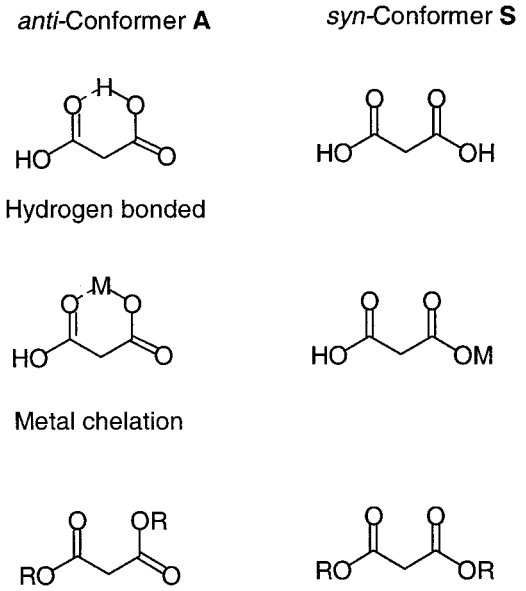


FIGURE 1 Assignment of the relative carbonyl group arrangements.

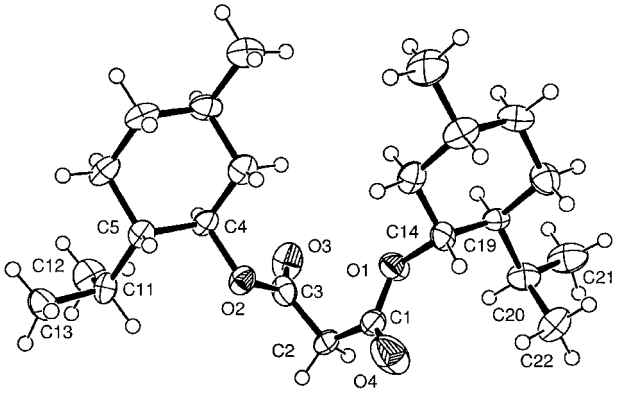
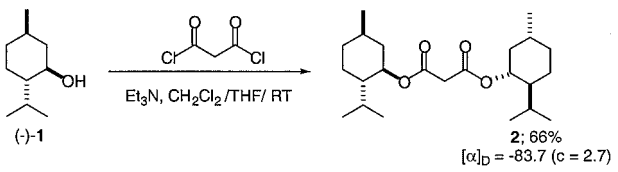


FIGURE 2 A view of molecule **2** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

(−)-menthol **1** as our ester scaffold as this would lead directly to the dimenthyl ester **2** without contamination resulting from the formation of other stereoisomers (Scheme 1). Treatment of commercially available malonyl dichloride to a stirred solution of naturally occurring (−)-menthol and Et_3N in dichloromethane gave the required C_2 symmetric (−)-dimenthyl malonate **2** as a cream coloured precipitate in 66% yield. After purification through flash column chromatography (on silica gel) and vapor re-crystallization (from hexane) gave a colorless needle-like crystal of **2**, the structure of which was determined by single crystal x-ray diffraction (Figure 2). The stereochemistry present in this derivative was determined by reference to (−)-menthol. On closer inspection of the unit cell, it was evident that the structure of menthyl malonate **2** was not C_2 symmetric in its solid phase, due to the nonequivalence of the carbonyl groups, C1=O4 and C3=O3. However, solution phase ^1H and ^{13}C NMR studies in $CDCl_3$ at room temperature have been shown to be consistent with C_2 symmetry due to the equivalence of the menthyloxycarbonyl motif. The overall unit cell was shown to *pseudo-*C_2 symmetric and contained two identical molecules of **2** as illustrated in Figure 2. All the substituents on the cyclohexyl ring are in the expected equatorial positions.



SCHEME 1 Preparation of Di-(−)-menthyl malonate **2**.

We were next concerned whether this dimenthyl malonate **2** existed as its related enol tautomer [15]. However, this was found not to be the case with a C1–C2–C3 bond angle of 111.5 (5)°, which is clearly representative of an sp^3 hybridised carbon atom with similar C1–C2 and C2–C3 bond lengths of 1.492 (7) and 1.497 (8) Å respectively (Table 1). This is consistent with the presence of a single carbonyl (C=O) stretching peak in the IR spectrum at 1720 cm^{-1} and the absence of an enolic hydrogen around 3000–3500 cm^{-1}. A striking feature of this molecule is the relative orientation of both carbonyl groups, C1=O4 and C3=O3; these are evidently twisted away from each other, as shown by torsion angles of 138.3 (6)° for O4–C2–C2–O3 and 102.6 (6)° for C1–C2–C3–O3 (Table 1). This may presumably be due to a combination of hyperconjugation effects associated with the hydrogen atoms at the C2 position with both carbonyl groups and a minimization of their relative dipole moments. This orientation can be seen further by a related twist involving the other oxygen atom in the ester motif; the torsion angles for O1–C1–C2–C3 and O1–C1–C2–C3 are −42.5 (6)° and −73.4 (6)°, respectively. In contrast, both ester motifs (C–O–C=O) exist in a predictable *s-cis* conformation [16] around the central single C–O bond and clearly strive for planarity [−0.8 (8)° for C14–O1–C1–O4 and −9.5 (7)° for C4–O2–C3–O3] through anomeric assistance. This type of *anti*-parallel alignment of the C=O bonds has previously been reported in the structural

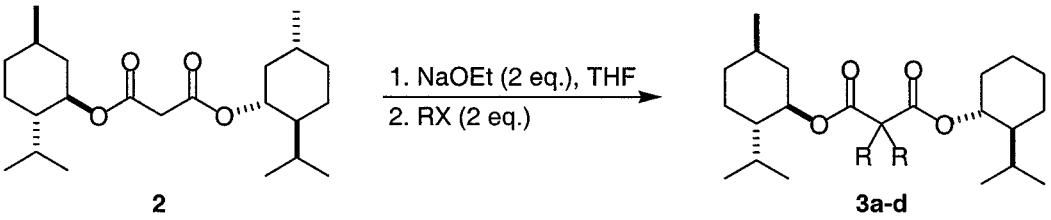
TABLE 1 Selected geometric parameters for dimenthyl malonate **2** (Å, °)

C2-C3	*1.497 (8)*	*C1-C2*	*1.492 (7)*
C14-O1-C1-O4	−0.8 (8)	C4-O2-C3-O3	−9.5 (7)
C14-O1-C1-C2	−180.0 (4)	C4-O2-C3-C2	−166.6 (4)
O4-C1-C2-C3	138.3 (6)	C1-C2-C3-O3	102.6 (6)
O1-C1-C2-C3	−42.5 (6)	C1-C2-C3-O2	−73.4 (6)
C12-C11-C5-C4	−62.9 (6)	C21-C20-C19-C14	173.5 (4)
C13-C11-C5-C4	172.7 (4)	C22-C20-C19-C14	−60.9 (6)

arrangement of malonic acids [17], diones [9a], triketones [18], diamides [19], and related malonate derivatives [20].

We next introduced some substitution at the carbon adjacent to both carbonyl groups to determine if this would alter the relative orientation of the carbonyl groups by lowing the amount of C–H hyperconjugation. We first synthesized the symmetrically di-substituted malonates derivatives **3a–d** since there would be no further complication with stereochemistry (Scheme 2). Treatment of a solution of (−)-dimenthyl malonate **2** in THF with an excess of NaOEt (2 equivalents), and subsequent alkylation of the intermediate enolate(s) gave the symmetrically substituted malonates **3a–d** as colorless oils in good chemical yield. These derivatives were shown to be C_2 symmetric by the equivalence of the menthyloxycarbonyl motifs–determined by ^{1}H and ^{13}C NMR spectroscopy. The presence of a single carbonyl stretching frequency at approximately 1718 cm^{-1} in the IR spectra further illustrates the carbonyl group (C=O) equivalence.

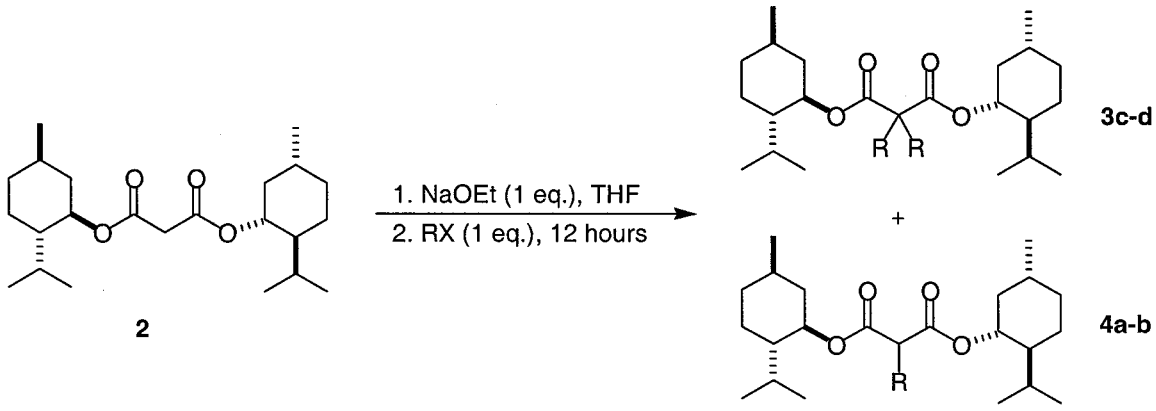
We next focused our attention on synthesizing a series of mono-substituted malonate derivatives **4a–d**. Deprotonation of the parent dimenthyl malonate **2** with NaOEt (1 equivalent) and addition of an appropriate alkylating reagent, such as benzyl bromide and allyl iodide, gave after stirring for 12 hours the required malonate **4a**+**b** in low yield (Scheme 3). However, repeating the same reaction with methyl and ethyl iodide gave surprisingly the di-substituted malonates **3c**+**d**. It appears that under these reversible conditions, the reaction is under thermodynamic control favoring the formation of the more substituted and more thermodynamically stable enolate **6**. Presumably, this is due to competitive deprotonation as a result of slow *C*-alkylation with a nonactivated electrophile (Scheme 4). However, if the reaction time was lowered to 3 hours and a sub-stoichiometric quantity of alkylating agent and base was used (0.5 equilvalent), the required kinetic mono-substituted malonates **4c–d** could exclusively be formed (Scheme 5). However, for activated electrophiles reagents, such as allyl bromide and benzyl bromide, the yields were found to be slightly lower than that for nonactivated electrophiles. This is not that surprising since it has previously been documented [21] that activated electrophiles prefer *O*-alkylation of enolates (derived from 1,3-dicarbonyl derivatives) to give enol ethers rather than traditional *C*-alkylation [22]. We next turned our attention to the synthesis of unsymmetrical di-substituted



2 **3a-d**

Entry	Starting material	RX	Product	$[\alpha]_D$	Yield
1	**2**	$PhCH_2Br$	**3a**	−44.2 (c = 9.7)	42%
2	**2**	CH_2CHCH_2I	**3b**	−44.6 (c = 3.1)	63%
3	**2**	CH_3CH_2I	**3c**	−56.8 (c = 8.1)	70%
4	**2**	CH_3I	**3d**	−61.0 (c = 3.7)	73%

SCHEME 2 Synthesis of symmetrically di-substituted di-(−)-menthyl malonates **3a–d**.

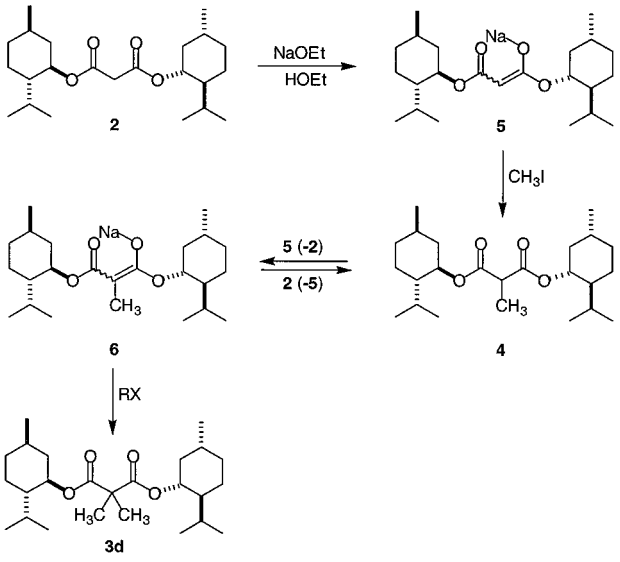


Entry	Starting material	RX	Product	$[\alpha]_D$	Yield
1	**2**	$PhCH_2Br$	**4a**	−61.1 (c = 2.0)	28%
2	**2**	CH_2CHCH_2I	**4b**	−67.9 (c = 2.6)	37%
3	**2**	CH_3CH_2I	**3c**	−56.8 (c = 8.1)	21%
4	**2**	CH_3I	**3d**	−61.0 (c = 3.7)	30%

SCHEME 3 Attempted synthesis of mono-substituted di-(−)-menthyl malonates **4a–d**.

malonate derivatives **7** and **8** (Scheme 6). We chose to alkylate our existing benzyl-substituted malonate **4a** using nonactivated electrophiles (e.g., methyl and ethyl iodide) to ensure efficient *C*-alkylation. Treatment of **4a** with NaOEt and addition of an excess of CH_3I and CH_3CH_2I (16–25 equivalents) gave the corresponding methylbenzyl and ethylbenzyl malonates derivatives **7** and **8** in good yield.

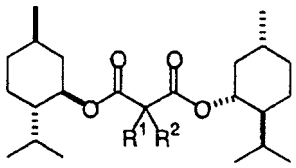
Introduction of a prostereogenic position adjacent to both menthyl motifs by single alkylation (e.g., to give **4a**) or by sequential addition of two different alkylating reagents (e.g., to give **7**) causes both menthyloxycarbonyl groups to be nonequilivalent. This effect can easily be seen in the ^{13}C NMR spectra due to the presence of two carbonyl (C=O) signal (at approximately δ 169 ppm), as well as up to 20 carbon atoms associated with both menthyl groups. It is rather interesting to note that the carbonyl (C=O) stretching frequencies in the IR spectra fall into two categories (Table 2): those for mono-substituted malonates **4a–d** give rise to two distinct sharp carbonyl (C=O) stretching frequencies at 1728 and 1745 cm^{-1} due to the nonequivalence of the C=O groups, whereas the unsymmetrically di-substituted derivatives **7** and **8** gave a broad stretching frequency between 1716–1724 cm^{-1}. All samples were purified through flash column chromatography (on silica gel) and vapor re-crystallized (from hexane). However, only the benzyldimenthyl malonate **4a** and the related methylbenzyldimenthyl malonate **7** gave sufficiently good crystals for x-ray diffraction.



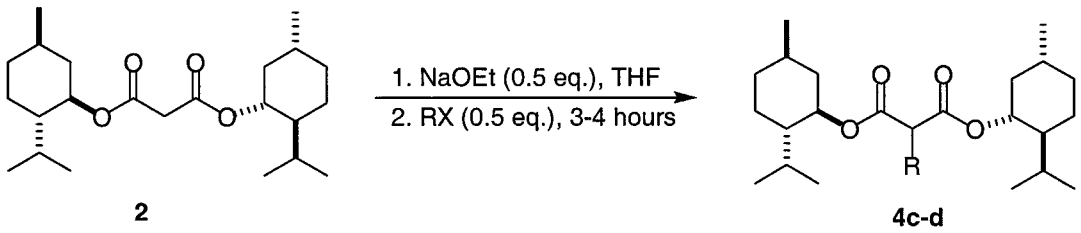
SCHEME 4 Synthesis of disubstituted di-(−)-menthyl malonate **3d**.

X-ray diffraction of benzyldimenthyl malonate **4a** revealed the structure illustrated in Figure 3. From this structure determination it is clear that both carbonyl groups (C9=O9 and C20=O20) have a *syn*-orientation (as illustrated by the torsion angles for O9–C9–C1–C20 and O20–C20–C1–C9 of −56.9 (3)° and 115.2 (3)°, respectively) rather than being oriented away from each other as in the case for the parent dimenthyl malonate **2** (Table 3). This molecule is not an enol derivative, with bond angles of 109.11 (19)° and 110.82 (19)° for C2–C1–C9

TABLE 2 Carbonyl infrared stretching frequencies for malonates **2**, **3a–d**, **4a–d**, **7** and **8**

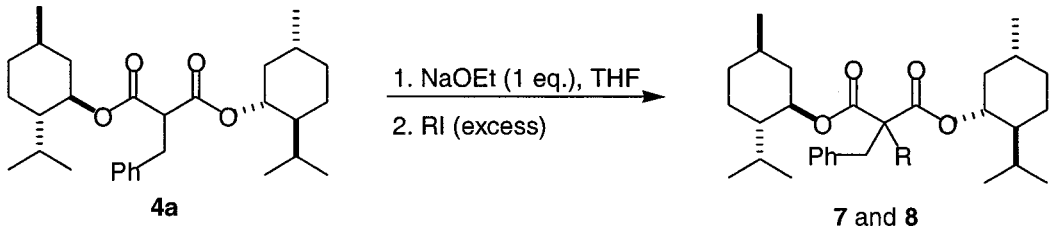


Entry	*Product*	R^1	R^2	ν_{max} (C=O)/cm^{-1}
1	**2**	H	H	1720
2	**3a**	$PhCH_2$	$PhCH_2$	1718
3	**3b**	CH_2CHCH_2	CH_2CHCH_2	1716
4	**3c**	CH_3CH_2	CH_3CH_2	1716
5	**3d**	CH_3	CH_3	1720
6	**4a**	$PhCH_2$	H	1728, 1745
7	**4b**	CH_2CHCH_2	H	1728, 1745
8	**4c**	CH_3CH_2	H	1728, 1745
9	**4d**	CH_3	H	1728, 1745
10	**7**	$PhCH_2$	CH_3	1724
11	**8**	$PhCH_2$	CH_3CH_2	1718



Entry	Starting material	RX	Product	$[\alpha]_D$	Yield
1	**2**	CH_3CH_2I	**4c**	−64.8 (c = 1.6)	61%
2	**2**	CH_3I	**4d**	−73.5 (c = 1.8)	75%

SCHEME 5 Synthesis of mono-substituted di-(−)-menthyl malonates **4c–d** under kinetic control.



Entry	Starting material	RI	Product	$[\alpha]_D$	Yield
1	**4a**	CH_3I	**7**	−49.2 (c = 1.8)	66%
2	**4a**	CH_3CH_2I	**8**	−47.8 (c = 3.0)	79%

SCHEME 6 Synthesis of unsymmetrically di-substituted di-(−)-menthyl malonates **7** and **8**.

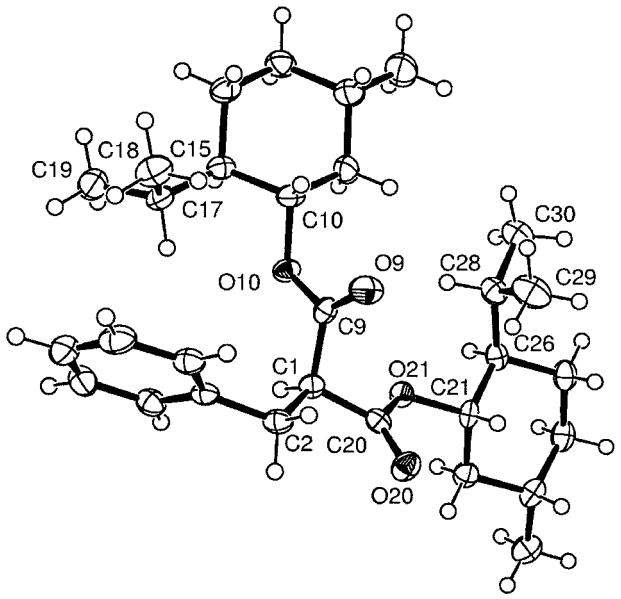


FIGURE 3 A view of molecule **4a** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

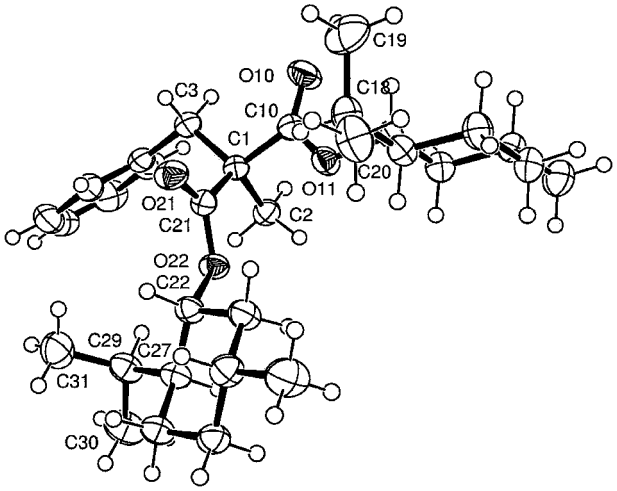


FIGURE 4 A view of molecule **7** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

and C2–C1–C20, respectively, and with similar C1–C9 and C1–C20 bond lengths of 1.520 (3) and 1.511 (3)Å, respectively. This particular *syn*-arrangement of the carbonyl groups is also present in the structure obtained from x-ray diffraction of benzylmethyl malonate **7** (Figure 4); these are oriented toward each other as shown by the torsion angles of −140.92 (16)° for O10–C10–C1–C21 and 68.25 (18)° for O21–C21–C1–C10 (Table 4). It is interesting to note, that enol formation cannot occur in this case and the associated C1–C21 and C1–C10 bond lengths [1.529 (2)Å and 1.529 (2)Å, respectively] were found to be similar to **2** and **4a** in which enol formation could have potentially occurred.

In all cases studied so far, we have found the menthyloxycarbonyl motif to be surprisingly uniform in its structural conformation. All the substituents on the cyclohexyl ring are in the expected equatorial positions. The isopropyl group [–$CH(CH_3)_2$] is oriented so the smaller C–H bond is *syn*-planar with the adjacent C–O single bond to avoid steric repulsion. The ester motif [OC–C=O] is predictably in its *s-cis* conformation, and the carbonyl group (C=O) was arranged parallel to the adjacent H–CO bond of the cyclohexyl ring. X-ray diffraction of these dimenthyl malonate derivatives **2, 4a** and **7** has revealed that the menthyloxycarbonyl motif behaves similarly and that the substitution at the central carbon (to which they are joined) is responsible for their structural characteristics. These structural feature has been found to be present in all cases so far examined [23]. The relative orientation of the C=O bonds has been shown to be *anti*-planar for menthyl malonate **2** and *syn*-planar for the substituted cases, benzylmenthyl and benzylmethylmenthyl malonate **4a** and **7**, respectively. These types of alignment has previously been reported in the structural arrangement of related malonate derivatives [4,9–11]. However, this carbonyl alignment appears to be unimportant with respect to the layered arrangement throughout the crystal structure, which appear as an AB arrangement

TABLE 3 Selected geometric parameters for benzyl dimenthyl malonate **4a** (Å, °)

C9-C1	1.520 (3)	C1-C20	1.511 (3)
C2-C1-C9	109.11 (19)	C2-C1-C20	110.82 (19)
C10-O10-C9-O9	−2.8 (3)	C21-O21-C20-O20	−9.2 (3)
C10-O10-C9-C11	175.3 (18)	C21-O21-C20-C1	170.15 (18)
O9-C9-C1-C20	−56.9 (3)	O20-C20-C1-C9	115.2 (3)
O10-C9-C1-C20	124.9 (2)	O21-C20-C1-C9	−64.1 (2)
C18-C17-C15-C10	72.3 (2)	C30-C28-C20-C21	−176.6 (6)
C19-C17-C15-C10	−163.22 (19)	C29-C28-C26-C21	57.3 (3)
C2-C1-C9-O9	64.5 (3)	C2-C1-C20-O20	−5.2 (3)

TABLE 4 Selected geometric parameters for benzylmethyl dimenthyl malonate **7** (Å, °)

C1-C21	1.529 (2)	C1-C10	1.531 (2)
C3-C1-C21	109.98 (12)	C3-C1-C10	109.49 (12)
C11-O11-C10-O10	−8.02 (2)	C22-O22-C21-O21	−4.8 (2)
C11-O11-C10-C1	167.78 (12)	C22-O22-C21-C1	165.07 (11)
O10-C10-C1-C21	−140.92 (17)	O21-C21-C1-C10	68.25 (18)
O11-C10-C1-C21	43.34 (16)	O22-C21-C1-C10	−111.64 (13)
C19-C18-C16-C11	−61.2 (2)	C30-C29-C27-C22	169.00 (14)
C20-C18-C16-C11	173.82 (14)	C31-C29-C27-C22	−65.53 (18)
C3-C1-C10-O10	−21.7 (2)	C3-C1-C21-O21	−50.65 (19)

due to the presence of a local pseudo-twofold axis present within the unit cell. This layered sequence is positioned in an ABAB arrangement with the layer B positioned anti-parallel to layer A.

EXPERIMENTAL

All solvents were distilled before use. Tetrahydrofuran (THF) and ether were freshly distilled from sodium wire using benzophenone as the indicator. Triphenylmethane was used as the indicator for THF. All reactions were carried out under nitrogen using oven-dried glassware. Flash column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Thin layer chromatography (TLC) was carried out on commercially available precoated plates (Merck Kieselgel $60F_{254}$ silica). Proton and carbon NMR spectra were recorded on a JEOL EX 270 and Bruker AM 250 fourier transform spectrometer (using an internal deuterium lock). Chemical shifts are quoted in parts per million downfield from tetramethylsilane. Carbon NMR spectra were recorded with broad proton decoupling. Infrared spectra were recorded on a Shimadzu 8300 FTIR machine, and mass spectra were recorded on a Kratos 50MSTC machine using a DS503 data system for high-resolution analysis.

Di-(−)-menthyl Malonate 2

Malonyl dichloride (5.0 g, 3.45 ml, 35.5 mmol) was slowly added to a stirred solution of triethylamine (7.2 g, 9.90 ml, 70.9 mmol) and (−)-menthol **1** (11.1 g, 70.9 mmol) in dichloromethane (100 ml) and the resulting solution was stirred for 1 h. The reaction was quenched slowly with water (30 ml) and the organic layer was extracted with diethyl ether (3 × 50 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-ether (19:1) to give the malonate **2** [24] (9.0 g, 66%) as light cream solid. This solid was recrystallized in hexane to give white needle crystals; mp = 54–55°C; R_F [light petroleum (40–60°C):ether (19:1)] 0.75; ν_{max} (film)/cm^{-1} 1725 (CO); $[\alpha]_D$ −83.7 (c 2.7 in $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 4.8 (2H, td, *J* 10.8 and 4.4, CHO), 3.36 (2H, s, CH_2CO), 2.15–0.85 (18H, m, 6 × CH_2 and 6 × CH), 1.1–0.95 (6H, m, 2 × CH_3) and 0.85 (3H, d, *J* 7.0, CHC*H*$_3$); δ_C (67 MHz, $CDCl_3$) 166.2, 75.5, 46.9, 42.4, 40.7, 34.2, 31.4, 26.1, 23.4, 22.0, 20.8 and 16.3 (Found M^+ 381.3017. $C_{23}H_{41}O_4$ requires M^+, 381.3005); *m/z* 381 (80%, M) and 243 (100, M−$C_{10}H_{18}$).

Di-(−)-menthyl Dibenzylmalonate 3a

Di-menthyl malonate **2** (0.5 g, 1.31 mmol) was added slowly to a stirred solution of sodium ethoxide (0.17 g, 2.62 mmol) in THF (100 ml). The resulting solution was stirred for 1 hour. Benzyl bromide (0.44 g, 2.62 mmol) was added and the reaction mixture was stirred for a further 3 hours. The reaction was quenched with water (30 ml) and the organic layer was extracted with diethyl ether (3 × 50 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-ether (19:1) to give the malonate **3a** (0.31 g, 42%) as a colorless oil; R_F [light petroleum (40–60°C):ether (19:1)] 0.80; ν_{max} (film)/cm^{-1} 1718 (CO); $[\alpha]_D$ −44.2 (c 9.7 in $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 7.26–7.10 (5H, m, Ph), 4.72 (1H, td, *J* 10.6 and 4.4, CHO), 3.25 (2H, AB quartet, CH_2Ph), 2.04–0.70 (18H, m, 6 × CH_2 and 6 × CH), 0.78 (3H, d, *J* 7.5, C*H*$_3$CH), 0.80 (3H, d, *J* 7.5, C*H*$_3$CH) and 0.75 (3H, d, *J* 7.2, C*H*$_3$CH); δ_C (67 MHz, $CDCl_3$) 171.0, 136.5, 130.5, 130.3, 128.8, 128.4, 128.1, 126.7, 75.7, 47.0, 46.7, 40.5, 40.4, 40.2, 38.6, 34.6, 34.2, 31.3,

25.4, 22.9, 22.0, 21.0, 15.9 (Found MH^+, 560.3963. $C_{37}H_{53}O_4$ requires 560.3944); *m/z* 561 (15%, MH) and 423 (100, M–$C_{10}H_{18}$).

Di-(−)-menthyl Diallylmalonate 3b

In the same way as di-(−)-menthyl dibenzylmalonate **3a**, malonate **2** (1.50 g, 3.94 mmol), sodium ethoxide (0.53 g, 7.88 mmol) and allyl bromide (0.95 g, 7.88 mmol) gave, after column chromatography on a silica gel the malonate **3b** (1.14 g, 63%) as a colourless oil; R_F [light petroleum (40–60°C):ether (19:1)] 0.80; ν_{max} (film)/cm^{-1} 1716 (CO); $[\alpha]_D$ −44.6 (c 3.1 in $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 5.60 (1H, m, C*H*=CH_2), 5.1 (2H, AB quartet, CH=CH_2), 4.68 (1H, td, *J* 10.8 and 4.8, CHO), 2.65 (2H, AB quartet, CH_2CH=CH_2), 2.05–0.80 (18H, m, 6 × CH_2 and 6 × CH), 0.90–0.85 (6H, m, 2 × CH_3), and *J* 7.5, CH_3CH) and 0.73 (3H, d, *J* 7.2, CH_3CH) (Found MH^+, 461.3639. $C_{29}H_{49}O_4$ requires 461.3631); *m/z* 461 (40%, MH) and 323 (100, M–$C_{10}H_{18}$).

Di-(−)-menthyl Diethylmalonate 3c

In the same way as di-(−)-menthyl dibenzylmalonate **3a**, malonate **2** (1.0 g, 2.63 mmol), sodium ethoxide (0.34 g, 5.26 mmol) and ethyl iodide (0.82 g, 5.26 mmol) gave, after column chromatography on a silica gel the malonate **4c** (0.80 g, 70%) as a colourless oil; R_F [light petroleum (40–60°C):ether (19:1)] 0.80; ν_{max} (film)/cm^{-1} 1716 (CO); $[\alpha]_D$ −56.8 (c 8.1 in $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 4.66 (1H, td, *J* 10.8 and 4.8, CHO), 2.05–0.80 (18H, m, 6 × CH_2 and 6 × CH), 1.95 (4H, q, *J* 7.2, 2 × C$H_2$$CH_3$), 0.90–0.85 (6H, m, 2 × CH_3), 0.80 (6H, t, *J* 7.2, 2 × CH_2CH_3), and 0.73 (3H, d, *J* 7.2, CH_3CH); δ_C (67 MHz, $CDCl_3$) 171.4, 74.9, 58.9, 46.9, 40.7, 34.3, 31.3, 25.7, 24.0, 22.9, 22.0, 20.9, 15.7 and 8.1 (Found MH^+, 437.3611. $C_{27}H_{49}O_4$ requires 437.3631); *m/z* 437 (40%, MH) and 299 (100, M–$C_{10}H_{18}$).

Di-(−)-menthyl Dimethylmalonate 3d

In the same way as di-(−)-menthyl dibenzylmalonate **3a**, malonate **2** (0.29 g, 0.76 mmol), sodium ethoxide (52 mg, 0.76 mmol) and methyl iodide (0.11 g, 0.76 mmol) gave, after column chromatography on a silica gel the malonate **3d** (0.26 g, 73%) as a colourless oil; R_F [light petroleum (40–60°C):ether (19:1)] 0.60; ν_{max} (film)/cm^{-1} 1720 (CO); $[\alpha]_D$ −61.0 (c 3.7 in $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 4.66 (1H, td, *J* 10.8 and 5.1, CHO), 2.05–0.80 (18H, m, 6 × CH_2 and 6 × CH), 1.60 (6H, s, 2 × CH_3), 0.93 (3H, d, *J* 7.1, CH_3CH), 0.85 (3H, t, *J* 7.4, CH_3CH) and 0.75 (3H, d, *J* 7.3, CH_3CH); δ_C (67 MHz, $CDCl_3$) 172.5, 75.0, 50.2, 47.0, 40.7, 34.3, 31.3, 25.9, 23.1, 22.8, 22.0, 20.8 and 16.0. (Found MH^+, 409.3300. $C_{25}H_{45}O_4$ requires 409. 3318); *m/z* 409 (40%, MH) and 271 (100, M–$C_{10}H_{18}$).

Di-(−)-malonate Benzylmalonate 4a

Di-menthyl malonate **2** (18.5 g, 48.7 mmol) was added slowly to a stirred solution of sodium ethoxide (3.15 g, 48.7 mmol) in THF (100 ml). The resulting solution was stirred for 1 hour. Benzyl bromide (3.15 g, 48.7 mmol) was added and the reaction mixture was stirred for a further 3 hours. The reaction was quenched with water (30 ml) and the organic layer was extracted with diethyl ether (3 × 50 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with light petroleum (b.p. 40–60°C)-ether (19:1) to give benzyl malonate **4a** (6.7 g, 29%) as a white powder, which was recrystallized from cold hexane to give white needles; mp = 82–84°C; R_F [light petroleum (40–60°C):ether (19:1)] 0.75; ν_{max} (film)/cm^{-1} 1745 (CO) and 1728 (CO); $[\alpha]_D$ −61.1 (c. 2.0 in $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 7.29–7.15 (5H, m, Ph), 4.75–4.61 (1H, m, CHO), 3.60 (1H, t, *J* 7.2, C*H*CH_2CO), 3.23 (2H, dd AB quartet, *J* 7.8 and 3.5, CH_2Ph), 2.07–0.70 (18H, m, 6 × CH_2 and 6 × CH), 0.91 (3H, d, *J* 7.5, CH_3CH), 0.89 (3H, d, *J* 7.5, CH_3CH) and 0.62 (3H, d, *J* 7.0, CH_3CH); δ_C (67 MHz, $CDCl_3$) 168.6, 168.5, 138.0, 136.5, 130.3, 128.9, 128.4, 128.1, 126.8, 75.7, 75.4, 54.1, 47.0, 46.8, 40.6, 40.5, 40.3, 38.7, 34.6, 34.2, 31.3, 25.9, 25.7, 23.3, 23.1, 22.0, 21.9, 21.0, 20.9, 16.1 and 16.0 (Found MH^+, 471.3487. $C_{30}H_{47}O_4$ requires 471.3474); *m/z* 471 (10%, MH), 333 (60, M–$C_{10}H_{16}$) and 285 (100, M–$C_{11}H_{21}O_2$).

Di-(−)-menthyl Allylmalonate 4b

In the same way as di-(−)-menthyl benzylmalonate **4a**, malonate **2** (1.5 g, 3.9 mmol), sodium

ethoxide (0.26 g, 3.9 mmol) and allyl bromide (0.47 g, 3.94 mmol) gave, after column chromatography on a silica gel the allyl malonate **4b** (0.62 g, 37%) as an oil; R_F [light petroleum (40–60°C):ether (19:1)] 0.75; ν_{max} (film)/cm^{-1} 1745 (CO) and 1728 (CO); $[\alpha]_D$ −67.9 (c. 2.6 in $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 5.81 (1H, m, C*H*=CH_2), 5.10 (2H, m, CH=C*H*$_2$), 4.73 (2H, td, *J* 10.8 and 4.4, CHO), 3.39 (1H, t, *J* 7.6, COC*H*CH_2), 2.71–2.58 (2H, m, CH_2C*H*=CH_2), 2.05–0.70 (18H, m, 6 × CH_2 and 6 × CH), 0.90 (3H, d, *J* 7.5, C*H*$_3$CH), 0.88 (3H, d, *J* 7.5, C*H*$_3$CH) and 0.61 (3H, d, *J* 7.0, C*H*$_3$CH); δ_C (67 MHz, $CDCl_3$) 168.7, 168.5, 134.2, 117.3, 65.4, 52.1, 47.0, 46.9, 40.8, 40.6, 34.2, 32.8, 31.4, 26.1, 25.8, 23.3, 23.1, 22.0, 20.9, 20.8, 16.2, and 16.0 (Found MH$^+$, 421.3325. $C_{26}H_{45}O_4$ requires 421.3318); *m/z* 421 (25%, MH) and 283 (100, M−$C_{12}H_{18}$).

Di-(−)-menthyl Ethylmalonate 4c

In the same way as di-(−)-menthyl benzylmalonate **4a**, malonate **2** (0.5 g, 1.31 mmol), sodium ethoxide (44.7 mg, 0.65 mmol) and ethyl iodide (0.1 g, 0.65 mmol) gave the malonate **4d** (0.16 g, 61%) as a white powder, which was recrystallized from cold hexane to give white needles; mp = 74–75°C; R_F [light petroleum (40–60°C):ether (19:1)] 0.75; ν_{max} (film)/cm^{-1} 1745 (CO) and 1728 (CO); $[\alpha]_D$ −64.8 (c 1.6 in $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 4.72 (2H, td, *J* 10.8 and 4.4, CHO), 3.32 (1H, t, *J* 7.5, C*H*CH_2CO), 2.10–0.78 (18H, m, 6 × CH_2 and 6 × CH), 0.92 (3H, t, *J* 7.2, C*H*$_3$CH_2), 0.91 (3H, d, *J* 7.5, C*H*$_3$CH), 0.89 (3H, d, *J* 7.5, C*H*$_3$CH) and 0.75 (3H, d, *J* 7.0, C*H*$_3$CH); δ_C (67 MHz, $CDCl_3$) 169.2, 169.0, 75.2, 54.2, 47.0, 46.9, 40.8, 40.6, 34.3, 31.4, 26.2, 25.9, 23.4, 23.2, 22.2, 22.0, 16.2, 16.1 and 11.8 (Found MH$^+$, 409.3330. $C_{25}H_{45}O_4$ requires 409.3318); *m/z* 409 (55%, MH) and 271 (100, M−$C_{10}H_{17}$).

Di-Menthyl Methylmalonate 4d

In the same way as di-(−)-menthyl benzylmalonate **4a**, malonate **2** (0.5 g, 1.31 mmol), sodium ethoxide (44.7 mg, 0.65 mmol) and methyl iodide (93.2 mg 0.65 mmol) gave the malonate **4d** (0.18 g, 72%) as a colorless oil; R_F [light petroleum (40–60°C):ether (19:1)] 0.75; ν_{max} (film)/cm^{-1} 1745 (CO) and 1738 (CO); $[\alpha]_D$ −73.5 (c 1.8 in $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 4.72 (2H, td, *J* 10.8 and 1.6, CHO), 3.39 (1H, q, *J* 7.3, C*H*CH_3CO), 2.14–0.78 (18H, m, 6 × CH_2 and 6 × CH), 1.44 (3H, d, *J* 6.5, C*H*$_3$CH), 0.90 (3H, d, *J* 7.5, C*H*$_3$CH), 0.88 (3H, d, *J* 7.4, C*H*$_3$CH) and 0.78 (3H, d, *J* 6.9, C*H*$_3$CH); δ_C (67 MHz, $CDCl_3$) 169.9, 169.7, 75.2, 75.1, 47.0, 46.9, 40.7, 40.6, 34.3, 31.4, 26.2, 25.9, 23.4, 23.3, 22.0, 20.8, 20.7, 16.3, 16.1 and 13.6 (Found MH$^+$, 395.3163. $C_{24}H_{43}O_4$ requires 395.3161); *m/z* 395 (10%, MH), 379 (15, M−CH_3) and 257 (100, M−$C_{10}H_{17}$).

Di-(−)-menthyl Methylbenzylmalonate 7

In the same way as di-(−)-menthyl benzylmalonate **4a**, malonate **4a** (0.51 g, 1.07 mmol), sodium ethoxide (73 mg, 1.07 mmol) and methyl iodide (3.77 g, 26.6 mmol) gave, after column chromatography on a silica gel the malonate **7** (0.34 g, 66%) as a solid, which was recrystallized (in hexane) to give white needles; m.p. 83–85°C; R_F [light petroleum (40–60°C):ether (19:1)] 0.86; ν_{max} (film)/cm^{-1} 1724 (CO); $[\alpha]_D$ −49.2 (c 1.8 in $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 7.29–7.13 (5H, m, Ph), 4.77–4.65 (2H, m, CHO), 3.13 (2H, br s, AB quartet, CH_2Ph), 2.00–0.60 (18H, m, 6 × CH_2 and 6 × CH), 1.25 (3H, s, CH_3), 0.89 (3H, d, *J* 7.5, C*H*$_3$CH), 0.87 (3H, d, *J* 7.5, C*H*$_3$CH) and 0.62 (3H, d, *J* 7.1, C*H*$_3$CH); δ_C (67 MHz, $CDCl_3$) 171.7, 171.1, 136.4, 130.4, 130.3, 128.0, 126.7, 75.7, 55.3, 47.0, 46.9, 41.1, 40.5, 34.2, 31.3, 25.6, 23.1, 23.0, 22.0, 20.9, 20.8, 19.6 and 15.3 (Found MH$^+$, 485.3647. $C_{31}H_{49}O_4$ requires 485.3631); *m/z* 485 (25%, MH), 393 (M−CH_2Ph), 346 (100, M−$C_{12}H_{18}$) and 285 (100 − $C_{12}H_{24}O_2$).

Di-(−)-menthyl Ethylbenzylmalonate 8

In the same way as di-(−)-menthylbenzylmalonate **4a**, malonate **4a** (0.40 g, 869 μmol), sodium ethoxide (65 mg, 86.9 mmol) and ethyl iodide (1.94 g, 14.6 mmol) gave, after column chromatography on a silica gel the malonate **8** (0.34 g, 80%) as a colourless oil; R_F [light petroleum (40–60°C):ether (19:1)] 0.86; ν_{max} (film)/cm^{-1} 1718 (CO); $[\alpha]_D$ −47.8 (c 3.0 in $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 7.26–7.10 (5H, m, Ph), 4.72 (1H, td, *J* 9.6 and 3.4, CHO), 4.70 (1H, td, *J* 9.6 and 3.4, CHO), 3.25 (2H, br s, AB quartet, CH_2), 2.05–0.65 (18H, m, 6 × CH_2 and 6 × CH), 0.93 (3H, d, *J* 7.5, C*H*$_3$CH), 0.89 (3H, d, *J* 7.5, C*H*$_3$CH), 0.75 (3H, d, *J* 7.1, C*H*$_3$CH) and 0.69 (3H,

t, *J* 7.3, CH_3CH_2); 171.5, 171.3, 136.5, 130.2, 128.2, 126.7, 75.5, 66.0, 60.0, 57.1, 46.9, 40.5, 34.3, 34.2, 31.4, 25.5, 22.1, 21.1, 21.0, 15.9, 15.4 and 8.7. (Found MH^+, 499.3768. $C_{32}H_{51}O_4$ requires 499.3787); *m/z* 499 (50%, MH) and 361 (100, M–$C_{10}H_{18}$).

X-Ray Crystallography of Di-(−)-menthyl Malonate 2

The intensity data were collected at 180 k on a CAD-4 diffractometer using MoKα radiation (λ 0.71069 Å) with ω-2θ scans. All data were corrected for absorption by empirical methods (ψ scan) [25] and for Lorentz-polarization effects by XCAD4 [26]. The structures were solved by the heavy-atom method using the programs SHELXS-97 [27], and DIRDIF-99 [28] and refined anisotropically (nonhydrogen atoms) by full-matrix least-squares on F^2 using SHELXL-97 [28]. The H atom positions were calculated geometrically and refined with a riding model. In the final stage of refinement, data were correct for absorption by DIFABS [29]. The programs ORTEP-3 [30], PLATON [31] were used for drawing the molecules and WINGX [32] was used to prepare material for publication. All data relating to this single crystal X-ray structure have been deposited at the Cambridge Crystallographic Database: reference number CCDC 182024 [14].

X-Ray Crystallography of Benzyldi-(−)-menthyl Malonate 4a and Methylbenzyldi-(−)-menthyl Malonate 7

Data for benzyldi-(−)-menthyl malonate **4a** and methylbenzyldi-(−)-menthyl malonate **7** were collected at 120 and 150 k using a Nonius Kappa CCD area detector diffractometer mounted at the window of a molybdenum rotating anode generator (50 KV, 90 mA, $\lambda = 0.71069$ Å). The crystal to detector distance was 45 mm and ϕ and Ω scans (0.7° increments, 84 s exposure time) were carried out to fill the Ewald sphere. Data collection and processing were carried out using the programs COLLECT [33], DENZO [34] and maXus [35] and empirical absorption correction was applied using SORTAV [36]. The structure was solved by direct methods using SHELXS-97 [27] and refined anisotropically-(nonhydrogen atoms) by full-matrix least-squares on F^2 using the SHELXL-97 program [27]. The H atoms were calculated geometrically and refined with riding model. The program ORTEP-3 [31] was used for drawing the molecules and WINGX [32] was used to prepare material for publication. All data relating to these single crystal X-ray structures have been deposited at the Cambridge Crystallographic Database: reference number CCDC 188449 (for **4a**) and 188488 (for **7**).

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