STERICALLY CROWDED HEXAALKYL BENZENE-1,2,3,4,5,6-HEXAKIS-[α-(ALKOXYCARBONYL)PROPANOATES]. SYNTHESIS AND CONFORMATION ANALYSIS

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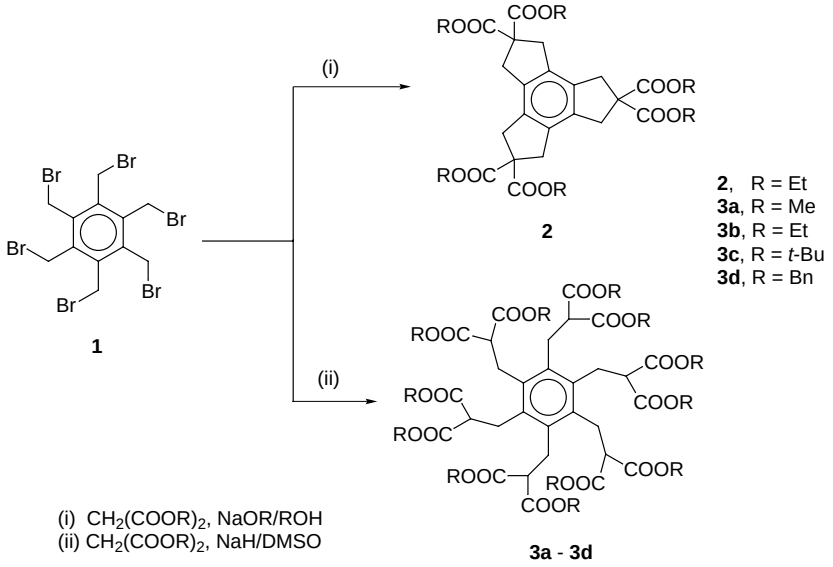
Dedicated to Professor Otakar Červinka on the occasion of his 75th birthday.

A selective hexa-fold monoalkylation of the malonester carbanion $^{(-)}CH(COOR)_2$ (R = Me, Et, *t*-Bu, Bn) with hexakis(bromomethyl)benzene afforded the title compounds **3** in a high-yield reactions. On subsequent replacement of the acid α-hydrogens with bulkier substituents, the title compounds **3**, R = Et, provided a broad variety of the α-X-persubstituted homologues and derivatives **4** (X = Me, Et, Bu, Oc, Bn, Br, N_3). The effect of the variable X substituent on conformation was investigated by single-crystal X-ray diffraction and compared with the results obtained by theoretical calculation.

Key words: Alkylations; Carbanions; Multiarmed compounds; Benzenes; Malonates; Molecular mechanics; Semiempirical calculations; X-Ray diffraction; Conformation analysis.

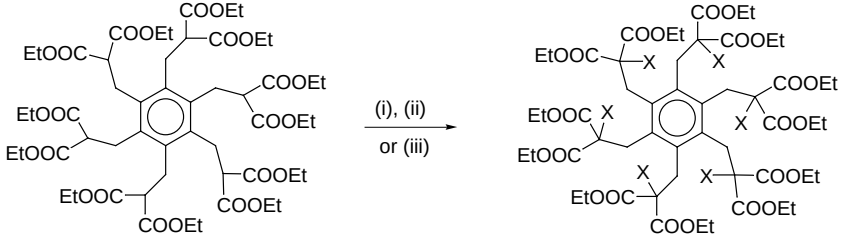
Mono- *vs* dialkylation selectivity of malonate carbanions is a problem of a considerable complexity[1,2]. As a part of our interest in multiarmed compounds[3], we have recently investigated the reaction of the easily accessible hexakis(bromomethyl)benzene **1** with the sodium salt of diethyl malonate. Unexpectedly, entirely different products have been found[4] to arise in the alkylation reaction performed in ethanol and in dimethyl sulfoxide. The tetracyclic product of a three-fold dialkylation **2** has prevailed in ethanol whereas the monocyclic product of a hexa-fold monoalkylation **3b** are dominated in DMSO (Scheme 1). In this way, an easy access has been pro-

vided, *via* **3b**, to a novel class of multiarmed compounds, potentially amenable to the synthesis of dendrimers[5] emanating from the hexabranched core.



SCHEME 1

Consideration of CPK models suggests that placing of the six malonester substituents on the periphery of the 1,2,3,4,5,6-hexamethylene substituted benzene implies steric crowding, which might hinder further synthetic transformations. In order to assess actual significance of such a steric crowding and its *modus operandi*, we have now systematically investigated the effect of steric bulk of individual malonester groups constituting the



(i) NaH/DMSO; (ii) alkyl halide (**4a** - **4e**) or $TosN_3$ (**4g**); (iii) Br_2/CCl_4, $(PhCO)_2O_2$ (**4f**)

SCHEME 2

hexamalonate molecule. First, we have varied the size of the alkoxycarbonyl groups in the malonester synthesis. Next, we have replaced the acid hydrogen in the malonester grouping with bulkier substituents of a varying size and examined the effect of this variation on the conformation of the target molecules (Scheme 2).

RESULTS AND DISCUSSION

Synthesis

In accord with the synthetic program outlined in the introduction, we have first investigated the effect of the alkoxy substituent (OR) in the hexa-fold monoalkylation of the malonester carbanion, $^{(-)}CH(COOR)_2$, with hexabromide **1** following Scheme 1 (NaH/DMSO). It has been found that a gradual increase in the carbanion bulkiness due to a stepwise lengthening and/or branching of the alkoxy group (OMe, OEt, OBn, O*t*-Bu) in the ester grouping does not substantially affect the rate of alkylation reaction. Under heating at 50 °C, the alkylation was completed within 2–3 h with the unbranched and within 5–6 h with the branched dialkoxycarbanions. The target compounds **3a**–**3d** were isolated invariably in very satisfactory yields (60% after several crystallizations) as sharp-melting crystals with melting points increasing with the size of the alkoxy group.

Next, synthesis of homologous hexamalonates **4a**–**4e**, peralkylated at the central carbon of the malonyl grouping, was systematically studied. Attempted alkylation of appropriately α-alkyl substituted malonester carbanions, $^{(-)}CX(COOR)_2$ (X = alkyl), with hexabromide **1** failed to afford the desired products. In contrast, an exhaustive alkylation of the complex carbanion generated from the parent α-unsubstituted hexamalonate **3b** (NaH/DMSO) with an appropriate alkyl iodide or bromide (Scheme 2) afforded the target α-peralkylated hexamalonates **4a**–**4e** in very satisfactory yields, mostly as sharp-melting crystals, with melting points increasing with the bulkiness of the alkyl substituent.

Complementarily with the α-peralkylation, also other α-persubstitutions were examined. Bromination of the parent hexamalonate **3b** with bromine in tetrachloromethane under reflux afforded cleanly the crystalline hexakis(α-bromomalonate) **4f** in a practically quantitative yield. Conversion of the perbromo substituted hexamalonate **4f** into the corresponding hexaazide **4g** on treatment with azide anion failed. However, transfer[6] of azide group from tosyl azide to the hexamalonate carbanion *in situ* gener-

ated from the hexamalonate **3b** (NaH/DMSO) produced cleanly the crystalline hexaazide **4g**.

Solid-State Conformation

Single crystals were obtained from the unsubstituted (**3b**) and α-X-persubstituted dodecaethyl hexamalonates **4a**–**4c** and **4f**, **4g** (X = Me, Et, Bu, Br and N_3, respectively) and their molecular structures were determined by X-ray diffraction. The perspective views of the individual molecules with atom labelling (ORTEP) are in Figs 1–6.

Common Features

In all instances (except one), the molecule consists of two symmetry-related halves. The hexasubstituted aromatic ring is always only slightly distorted; the bond lengths lie within 1.382–1.419 Å, the endocyclic bond angles within 119.1–120.5° and the maximum deviation of a ring atom from the least-square plane is 0.034 Å. Bond lengths and bond angles of the benzene ring substituents are also unexceptional.

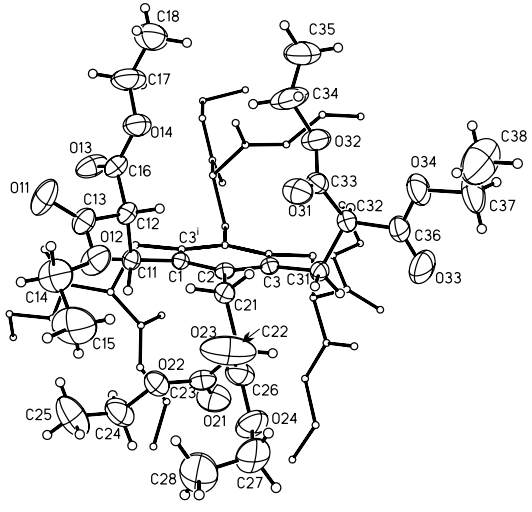


FIG. 1
Perspective view of **3b**. Thermal ellipsoids (30% probability level) and hydrogen atoms are only drawn for asymmetric part; symmetry code: i, 0.5 – *x*, 0.5 – *y*, –*z*

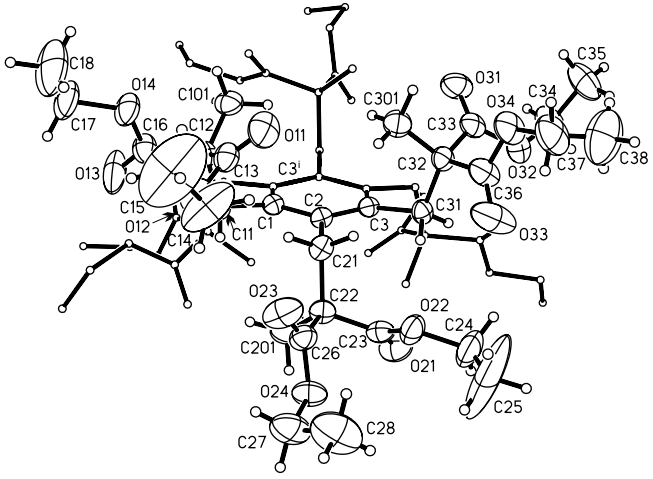


FIG. 2
Perspective view of **4a**. Thermal ellipsoids (30% probability level) and hydrogen atoms are only drawn for asymmetric part; symmetry code: i, *–x*, *–y*, 1 – *z*

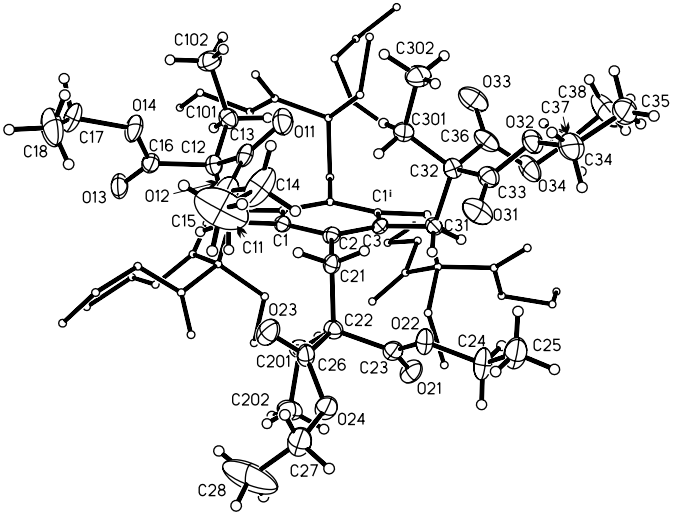


FIG. 3
Perspective view of one molecule of **4b**. Thermal ellipsoids (30% probability level) and hydrogen atoms are only drawn for asymmetric part; symmetry code: i, 1 – *x*, 1 – *y*, –1 – *z*. For the second molecule, add 3 to the first digit of atom label

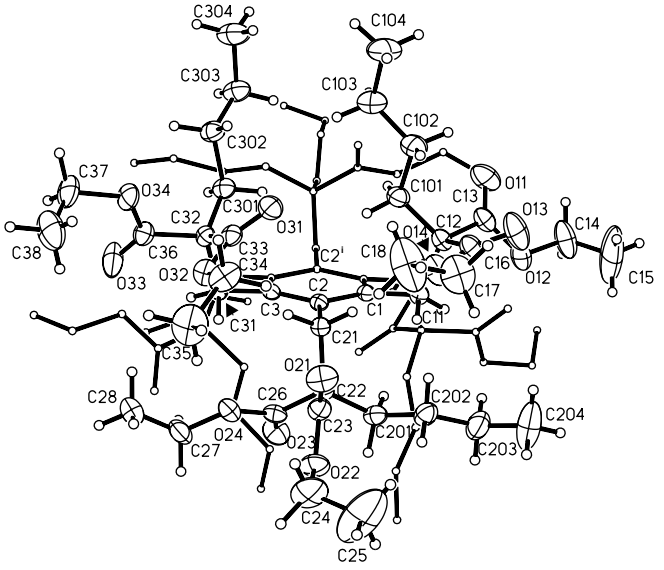


FIG. 4

Perspective view of **4c**. Thermal ellipsoids (30% probability level) and hydrogen atoms are only drawn for asymmetric part; symmetry code: i, *–x*, *–y*, 1 – *z*

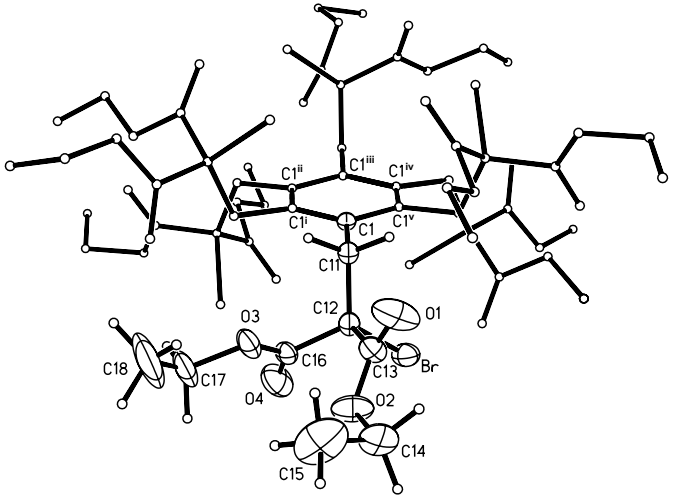


FIG. 5

Perspective view of **4f**. Thermal ellipsoids (30% probability level) and hydrogen atoms are only drawn for asymmetric part; symmetry code: i, *x*, *y* – *x*, *–z*; ii, *–y*, *–x*, *z*; iii, *–x*, *–y*, *–z*; iv, *–x*, *x* – *y*, *z*; v, *y*, *x*, *–z*

Conformational flexibility allows to release the steric crowding imposed by the six substituents. The primary release of the crowding is due to the alternate arrangement of the substituents up and down with respect to the central ring. Already the pivot carbon atoms C#1 (# represents the first digit in labels of atoms constituting the individual substituents: C*1*1, C*1*2…; C*2*1, C*2*2…; C*3*1, C*3*2…; *etc.*) are severely displaced up to 0.316(4) Å away from the aromatic plane in the direction of the whole substituent.

Proceeding further along the substituent, the C#2 atoms are tilted away from the ring two-fold axis passing through C#; the corresponding pseudotorsion angles[7] (which do not show any clear dependence on the variable X group) are summarized in Fig. 7. Figure 8 shows that the pivot atom of the X group is synclinal to synperiplanar relative to the C#–C#1 bond but, again, no clear dependence on the variable X group has been found.

Proceeding farther to the periphery of the molecules, the mutual conformation of the ethoxycarbonyl groups at the same substituent displays a distinct preference for antiperiplanar orientation along the link

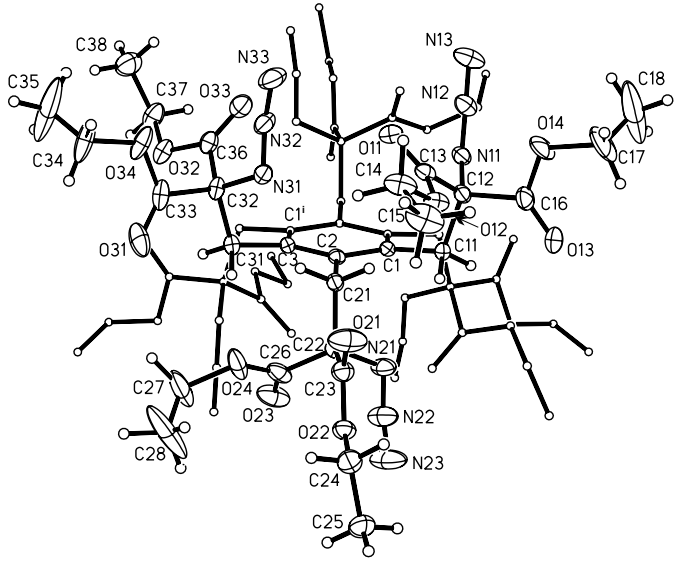


FIG. 6

Perspective view of one molecule of **4g**. Thermal ellipsoids (30% probability level) and hydrogen atoms are only drawn for asymmetric part; symmetry code: i, $-x - 1/2, -y + 1/2, 1 - z$. For the second molecule, add 3 to the first digit of atom label

O#1–C#3···C#6–O#3 (Fig. 9) but other arrangements are also observed. A characteristic feature of all the investigated molecules is a high flexibility of the terminal ethoxy groups which manifests itself primarily as large thermal displacement parameters of the methylene and especially of the methyl carbons for most of the ethoxy groups. While the methylene carbons of the terminal ethyls are usually coplanar with the carboxyl within

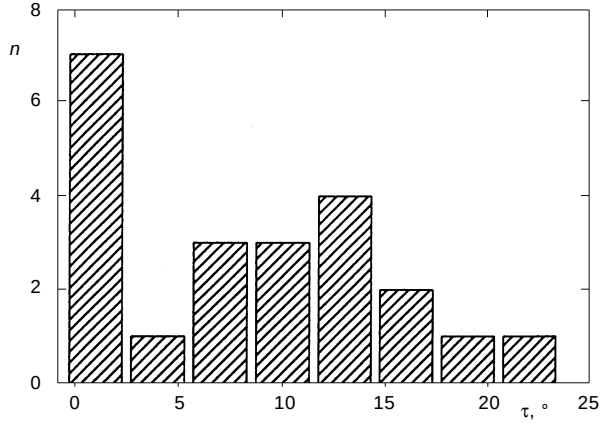


FIG. 7
Distribution of torsion angles C#′–C#–C#1–C#2 (for the meaning of symbols, see the text); *n* number of observations

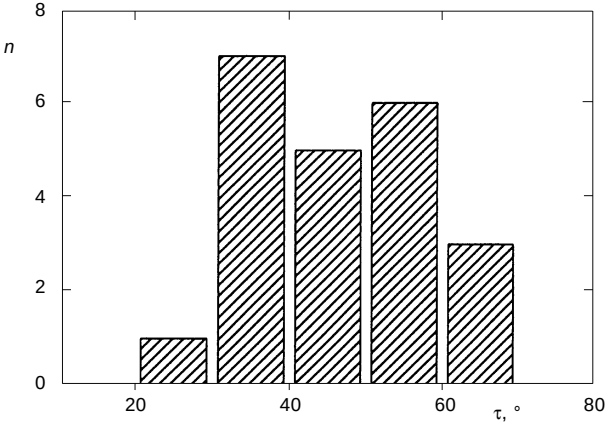


FIG. 8
Distribution of pseudotorsion angles C#–C#1–C#2–X; *n* number of observations

0.156 Å, there is a wide variety in orientation of the terminal methyls. The conformation and the degree of the thermal motion vary markedly from structure to structure and from one side chain to another but there is a significant preference for antiperiplanar and perpendicular arrangement of the terminal methyl in respect to the –C–O–CH_2– link (Fig. 10).

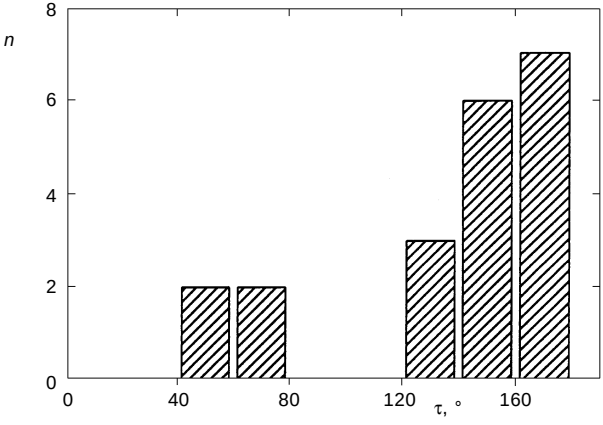


FIG. 9
Distribution of pseudotorsion angles O#1–C#3–C#6–O#3; *n* number of observations

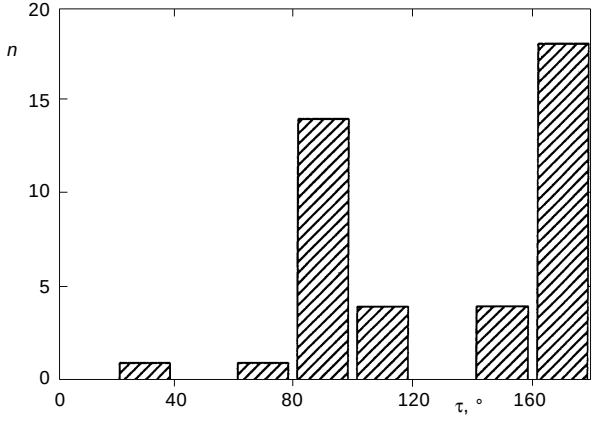


FIG. 10
Distribution of torsion angles of the COEt groups; *n* number of observations

Specific Features Imposed by the Variable X Group

Complexity of the ORTEP diagrams in Figs 1–6 complicates a systematic analysis of the conformational effect of the variable X group. The simplified diagrams which employ stick model type and experimental diffraction data omitting peripheral ethoxyl groupings as well as the conformationally insignificant hydrogen atoms have been therefore introduced.

A cursory inspection of the diagrams immediately shows that the mutual orientation of the X groups which are placed on the neighbouring arms depends markedly on the identity of the variable X group. The conformational effect is most clearly viewed looking along the central axis which is perpendicular to the aromatic ring of the investigated molecule (Figs 11–18).

It can be seen that in the unsubstituted (**3b**; X = H) as well as in the α-permethylated (**4a**; X = Me) hexamalonate, all the X substituents (above as well as below the aromatic ring) are displaced from the center of the molecule in the same (conrotatory) direction (Figs 11, 12).

With the α-perethylated homologue **4b**, the conformational situation is complicated by occurrence of two independent molecules in the unit cell differing from each other by orientation of α-ethyls with respect to the aromatic ring (pseudoaxial or pseudoequatorial). However, the mutual orientation of the ethyl groups is practically identical in both the two independent molecules (Figs 13, 14), being the same (conrotatory) as it was observed above for the lower homologues **3b** and **4a** (X = H and Me, respectively).

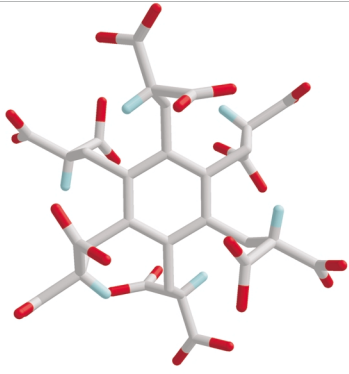


FIG. 11
Compound **3b** (X = H)

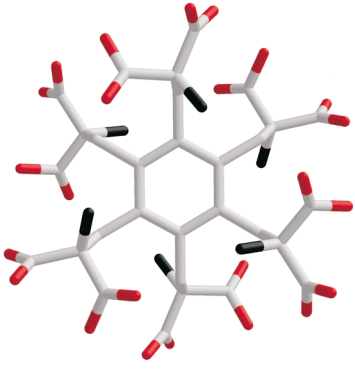


FIG. 12
Compound **4a** (X = Me)

The conformation of the α -perbutylated homologue **4c** (Fig. 15) resembles one independent molecule of the α-perethylated hexamalonate **4b** in the pseudoaxial orientation of the α-alkyl substituents with respect to the central aromatic plane. However, the mutual orientation of individual alkyls is different, two butyls placed in *para* positions being oriented disrotatory with respect to the remaining four (conrotatory) alkyl groups.

A quite analogous conformation exhibiting two disrotatory substituents in *para* position also occurs in the molecule of the α-perbrominated (X = Br) hexamalonate **4f** (Fig. 16). The conformational situation concerning the

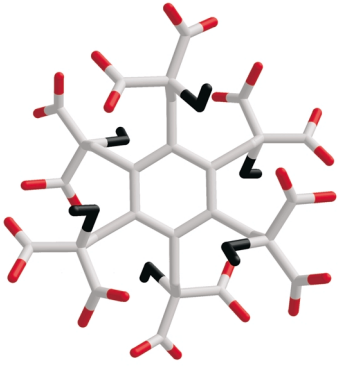


FIG. 13
Compound **4b** (X = Et), molecule 1

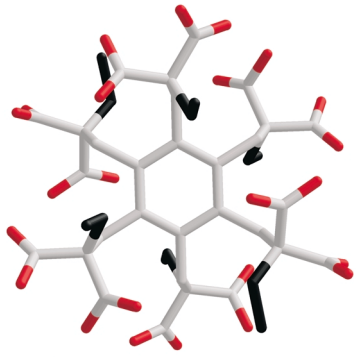


FIG. 14
Compound **4b** (X = Et), molecule 2

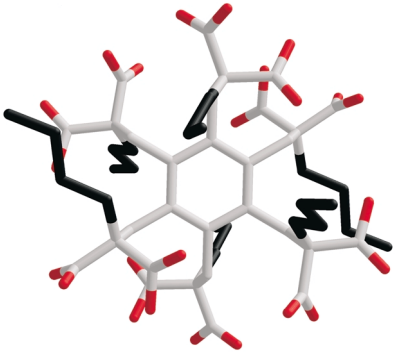


FIG. 15
Compound **4c** (X = Bu)

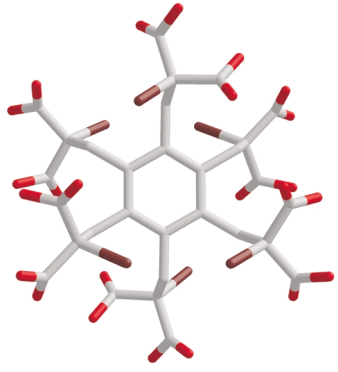


FIG. 16
Compound **4f** (X = Br)

α-perazido derivative **4g** is again complicated by the occurrence of two independent molecules in the unit cell. One molecule exhibits a conrotatory orientation of all azide groups (Fig. 17), resembling the **3b** and **4a**–**4b** homologues. In the other independent molecule, however, the conrotatory orientation involves only the azido groups which are placed at the alternating (1,3,5 or 2,4,6) arms. The neighbouring azido groups (on the 1,2; 3,4; 5,6 arms) exhibit, in a contrast, always the disrotatory orientation. In other words, the azido groups placed above and below the aromatic ring "rotate" in the opposite direction (Fig. 18).

The overall conformational effect of the variable X substituent is summarized schematically in Fig. 19.

Theoretical Calculations

Persubstituted 1,2,3,4,5,6-hexamethylenebenzenes $(RCH_2)_6C_6$ may exist in eight stereoisomeric forms **A**–**H** differing by the arrangement of the individual substituents above or below the central aromatic ring (Fig. 20). Intuitively, the lowest energy arrangement corresponds to the alternate "up-down" form **A**. The energy of the other conformers should increase gradually with the increasing number of syn interactions between the neighbouring substituents, being the highest for the "all-up" form **H**. Such a concept is supported in literature by the molecular mechanics calculation performed for hexaethylbenzene[8–11] **5** and hexakis(bromomethyl)benzene[12] **1**. At the same time, this concept agrees with experimental evidence based on

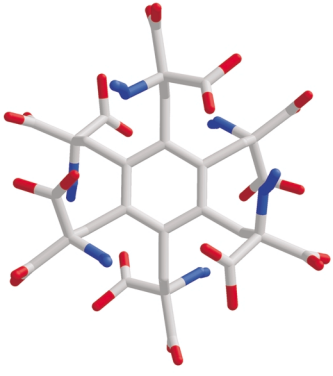


FIG. 17
Compound **4g** (X = N_3), molecule 1

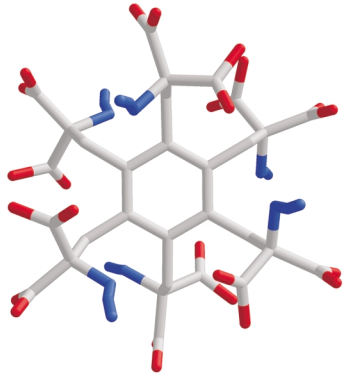
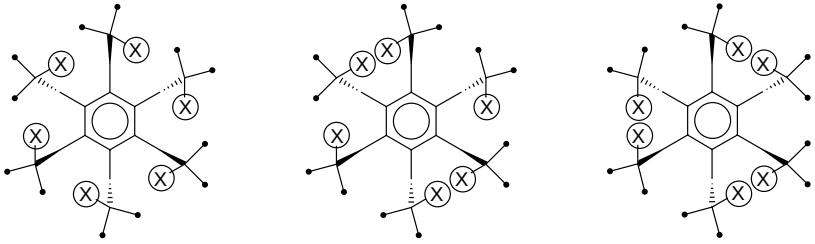


FIG. 18
Compound **4g** (X = N_3), molecule 2

the crystallographic analysis of these compounds[8,12]. Our present observation that the hexamalonates **3b** as well as **4a**–**4c** and **4f**, **4g** also exist exclusively (in crystals) in the alternate "up-down" conformation corro- borates the earlier evidence.

Complementally to the experimental study, we have attempted to calculate the energy difference between the extreme conformational arrange-



3b, X = H
4a, X = Me
4b, X = Et
4g/1, X = N_3

4c, X = n-Bu
4f, X = Br

4g/2, X = N_3

FIG. 19
Conformational effect of substituent X

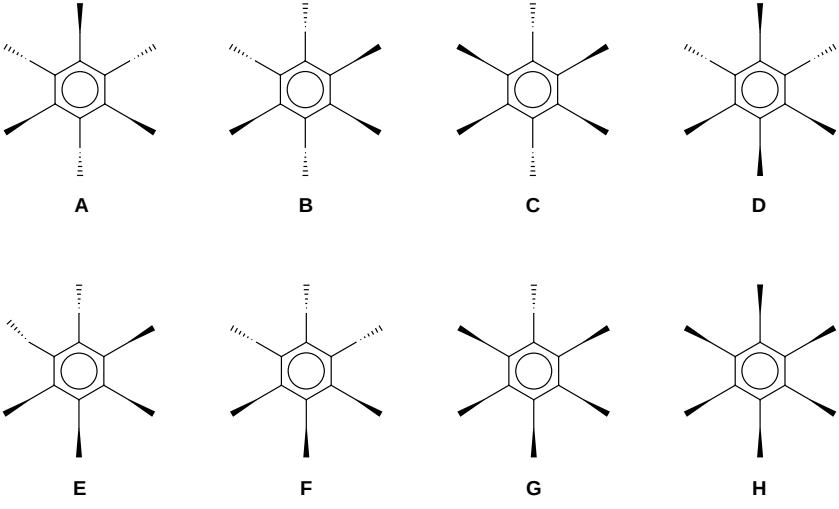


FIG. 20
Possible conformers of a persubstituted 1,2,3,4,5,6-hexamethylenebenzene differing in the arrangement of individual substituents above or below the central aromatic ring

ments **A** and **H** for two representative hexamalonates **3a** and **3c**. For sake of comparison, two semiempirical methods (PM3 (ref.[13]) and AM1 (ref.[14]), program MOPAC (ref.[15])) and also molecular mechanics (MM2 (ref.[16])) have been employed in the calculation. The calculation was extended at two earlier models **1** and **5** and the results have been summarized in Table I.

It has been found that MM2 calculation, although better justified only for the simple models **1** and **5**, leads to rational results also for the hexamalonates **3a** and **3c**, preferring invariably the alternate arrangement **A**. In contrast, the semiempirical (PM3) method failed in the calculation of the most simple model **5**, predicting, incorrectly, the energetical preference of "all-up" arrangement **H**. Insufficient description of weak hydrogen–hydrogen interactions representing here the major part of the calculated energy difference is probably the responsible factor. For the sterically more complex structures (**3a**, **3c** and **1**) the results of the all compared methods are in accord with the experimental evidence (preference of **A**).

Next, we have calculated the energy differences between the alternative conrotatory and disrotatory arrangement of the α-substituents in the investigated hexamalonate series. Employing the PM3 method, theoretical preference of the former over the latter arrangement was invariantly (with **3b**, **4a**, **4f** and **4g**) found. Only a slight energy difference (about 0.6 kcal/mol) between the two modes of the conrotatory arrangement of the azide substituents found in the solid-state structure of the perazido-substituted hexamalonate **4g** (Figs 17 and 18) has been calculated. In contrast, a very

TABLE I
Calculated energy differences ($\Delta E = E_A - E_H$) for several persubstituted 1,2,3,4,5,6-hexamethylenebenzenes in two extreme conformations **A** and **H** (see Fig. 20). Values from literature are given in parentheses

Compound	Calculated energy differences, kcal/mol		
	MM2 (ref.[16])	PM3 (ref.[13])	AM1 (ref.[14])
1	–10.8 (–11, ref.[12])	–3.8	–9.9
3a	–26.6	–32.9	–20.9
3c	–20.3	–27.2	–28.4
5	–9.3[a] (–9, ref.[8])	6.7	–7.0

[a] In *ab initio* calculation[17] –10.4 kcal/mol, 6-31G (d,p) basis set.

marked increase in energy of 17 kcal/mol has been calculated on going from the theoretical conrotatory minimum to the disrotatory arrangement (Fig. 16) occurring in the solid-state crystal structure of the perbromo substituted hexamalonate **4f**.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. ^{1}H NMR spectra were measured on a Varian Unity XL-200 spectrometer (200 MHz, FT mode) using tetramethylsilane as an internal standard (chemical shifts are given in ppm (δ-scale), coupling constants (*J*) are given in Hz). IR spectra (wavenumbers in cm^{-1}) were recorded on FTIR spectrometer Bruker IFS 88. Mass spectra were recorded on a ZAB-EQ (VG Analytical) instrument, for FAB techniques bis(2-hydroxyethyl) disulfide (DS) and dithiothreitol/dithioerythritol (DTT/DTE) as matrices were used. Thin-layer chromatography (TLC) was carried out on Kieselgel 60 F_{254} (Merck) plates. HPLC analyses were performed on an ECOM chromatograph with a UV detector operating at 254 nm. Dimethyl sulfoxide was dried over molecular sieves.

Unsubstituted Hexamalonates **3a**–**3d**. General Procedure

Sodium hydride (59% in mineral oil) was washed with light petroleum and suspended in dimethyl sulfoxide. An appropriate dialkyl malonate was added dropwise to the stirred slurry, followed (after 30 min) by hexabromide **1**. The mixture was heated 2–3 h (5 h with hexamalonates **3c** and **3d**) and the gradual disappearance of the bromomethyl groups was monitored using TLC (petroleum ether–ether–acetone–methanol 50 : 30 : 17 : 3; detection with 1% alcoholic solution of 4-(4-nitrobenzyl)pyridine at 100 °C followed by triethylamine). After completion of the reaction, the mixture was poured into water (ten-fold excess) and neutralized with dilute aqueous HCl. The resulting precipitate was sucked off, washed with water and petroleum ether, and crystallized. If the crude product did not precipitate (compound **3c**), it was isolated from the reaction mixture by extraction with ether. Purity of individual products was followed by HPLC analysis (Partisil 10 Silica, 250 × 4.6 mm column; petroleum ether–dioxane gradient; 1 ml/min).

Hexamethyl benzene-1,2,3,4,5,6-hexakis[α-(methoxycarbonyl)propanoate] (**3a**). Prepared from dimethyl malonate (23.78 g, 180 mmol), sodium hydride/oil suspension (5.69 g, 140 mmol) and hexabromide **1** (12.71 g, 20 mmol) in dimethyl sulfoxide (200 ml). The crude product was crystallized from methanol and recrystallized from ethyl acetate, m.p. 167–168 °C, yield 15.3 g (65%). For $C_{42}H_{54}O_{24}$ (942.9) calculated: 53.50% C, 5.77% H; found: 53.27% C, 5.69% H. MS (FAB, DS, $CHCl_3$), *m*/*z* (rel.%): 965 [$(M + Na)^+$, 10], 943 [$(M + H)^+$, 30], 811 (35). ^{1}H NMR ($CDCl_3$): 3.69 s, 36 H (12 × C**H**$_3$); 3.30–3.45 m, 18 H (6 × C**H**$_2$ + 6 × C**H**). IR (CCl_4): 3 031 m (ν_{as} CH_3); 2 956 m (ν_{as} CH_3, CH_2); 2 846 w (ν_s CH_2); 1 752 vs, 1 736 vs (ν C=O); 1 436 vs (δ_s CH_3); 1 488 w (ν ring).

Hexaethyl benzene-1,2,3,4,5,6-hexakis[α-(ethoxycarbonyl)propanoate] (**3b**). Prepared from diethyl malonate (51.18 g, 180 mmol), sodium hydride/oil suspension (5.69 g, 140 mmol) and hexabromide **1** (15.89 g, 25 mmol) in dimethyl sulfoxide (250 ml). The crude product was crystallized twice from ethanol and recrystallized from ether–petroleum ether, m.p. 170–172 °C (ref.[4] 168–170 °C), yield 21.5 g (77.5%). For $C_{54}H_{78}O_{24}$ (1 111.2) calculated: 58.36% C, 7.07% H; found: 58.74% C, 7.15% H. ^{1}H NMR and mass spectra in accord with ref.[4]. IR

(CCl_4): 2 983 m (ν_{as} CH_3); 2 930 w (ν_{as} CH_2); 2 908 w (ν_s CH_3); 2 873 w (ν_s CH_2); 1 752 vs, 1 735 vs (ν C=O); 1 369 m (δ_s CH_3); 1 281 s, 1 226 s.

Hexa-tert-butyl benzene-1,2,3,4,5,6-hexakis[α-(tert-butyloxycarbonyl)propanoate] (**3c**). Prepared from di-*tert*-butyl malonate (1.95 g, 9 mmol), sodium hydride/oil suspension (285 mg, 7 mmol) and hexabromide **1** (636 mg, 1 mmol) in dimethyl sulfoxide (10 ml). The crude product was washed with petroleum ether and crystallized from acetone–petroleum ether, m.p. 207–210 °C, yield 825 mg (57%). For $C_{78}H_{126}O_{24}$ (1 447.8) calculated: 64.71% C, 8.77% H; found: 64.84% C, 8.88% H. MS (FAB, DTT/DTE, $CHCl_3$), *m*/*z* (rel.%): 1 448 [$(M + H)^+$, 5], 1 402 (4), 1 345 (14), 1 223 (21), 1 168 (16), 1 089 (20), 1 051 (16), 949 (19), 883 (21), 817 (26), 775 (100), 757 (49), 713 (25), 731 (41), 671 (51), 655 (28), 608 (32), 569 (29), 525 (46). ^{1}H NMR ($CDCl_3$): 3.33 d, $^3J_{HH}$ = 6.1, 12 H (6 × C**H**$_2$); 3.11 t, $^3J_{HH}$ = 6.1, 6 H (6 × C**H**); 1.43 s, 108 H (36 × C**H**$_3$). IR (KBr): 2 981 s, 3 004 m (ν_{as} CH_3); 2 935 m (ν_{as} CH_2); 2 908 w, 2 892 w (ν_s CH_3); 2 872 w (ν_s CH_2); 1 745 vs, 1 728 vs (ν C=O); 1 480 m, 1 457 w (δ_{as} CH_3); 1 432 w (β_s CH_2); 1 394 m, 1 369 s (δ_s CH_3); 1 286 s, 1 257 s, 1 225 m, 1 137 vs, 1 056 w, 1 168 vs.

Hexabenzyl benzene-1,2,3,4,5,6-hexakis[α-(benzyloxycarbonyl)propanoate] (**3d**). Prepared from dibenzyl malonate (51.18 g, 180 mmol), sodium hydride/oil suspension (5.69 g, 140 mmol) and hexabromide **1** (12.71 g, 20 mmol) in dimethyl sulfoxide (200 ml). The crude product was crystallized twice from acetone, m.p. 145–146 °C, yield 16.23 g (87%). For $C_{114}H_{102}O_{24}$ (1 856.1) calculated: 73.77% C, 5.54% H; found: 73.82% C, 5.56% H. MS (FAB, DS, DMSO), *m*/*z* (rel.%): 1 856 (M^+, 5), 1 809 (8), 1 765 (5), 1 671 (7), 1 527 (6), 1 359 (10), 1 292 (9), 1 195 (10), 1 134 (45), 1 112 (100). ^{1}H NMR ($CDCl_3$): 7.20–7.16 m, 60 H (Ar-**H**); 5.11 d, $^2J_{AB}$ = 12.4, 12 H (6 × C**H**$_2$ ester); 4.94 d, $^2J_{AB}$ = 12.4, 12 H (6 × C**H**$_2$ ester); 3.53 m, 18 H (6 × C**H**$_2$ + 6 × C**H**). IR (KBr): 3 091 w, 3 064 w, 3 034 m (ν CH benzyl ester); 2 955 w (ν_{as} CH_2 benzyl ester); 2 894 w (ν_s CH_2 benzyl ester); 2 854 w (ν_s CH_2); 1 750 vs, 1 730 s (ν C=O); 1 609 w, 1 587 w, 1 498 w, 1 455 m (ν ring benzyl ester); 1 434 w (β_s CH_2); 1 377 w (β_s CH_2 benzyl ester); 1 332 w (γ_s CH_2); 1 284 s, 1 228 s, 1 220 s, 1 188 s, 1 166 m, 1 147 m, 1 081 w, 1 066 w, 992 w, 951 w.

α-Peralkylation of Unsubstituted Hexamalonate **3b**. General Procedure

Sodium hydride (59%; in mineral oil) was washed with petroleum ether and suspended in dimethyl sulfoxide. Hexamalonate **3b** was added dropwise to the stirred slurry followed (after 60 min) by an appropriate alkyl halide. The resulting mixture was heated at 50 °C for 4 h (with alkyl iodides) or at 80 °C for 7 h (with benzyl bromide). The volatiles were evaporated, the residue was poured into water and neutralized with dilute aqueous HCl. The resulting precipitate was sucked off, washed with water and petroleum ether, and the product was crystallized.

Hexaethyl benzene-1,2,3,4,5,6-hexakis[α-(ethoxycarbonyl)-α-methylpropanoate] (**4a**). Prepared from hexamalonate **3b** (2.22 g, 2 mmol), sodium hydride/oil suspension (732 mg, 18 mmol) and methyl iodide (4.26 g, 30 mmol) in dimethyl sulfoxide (32 ml). The crude product was crystallized twice from ethanol and subsequently from ether–petroleum ether, m.p. 140–142 °C, yield 1.79 g (75%). For $C_{60}H_{90}O_{24}$ (1 195.4) calculated: 60.29% C, 7.59% H; found: 59.95% C, 7.69% H. MS (FAB, DS, $CHCl_3$), *m*/*z* (rel.%): 1 218 [$(M + Na)^+$, 8], 1 196 [$(M + H)^+$, 10], 1 182 (4), 1 167 (3), 1 154 (3), 1 130 (4), 1 076 (3), 1 022 (100), 1 008 (25), 994 (17), 980 (11). ^{1}H NMR ($CDCl_3$): 4.27–4.15 m, 24 H (12 × OC**H**$_2$); 3.45 s, 12 H (6 × C**H**$_2$); 1.23 t, $^3J_{HH}$ = 7, 36 H (12 × OCH_2C**H**$_3$); 1.02 s, 18 H, (6 × C**H**$_3$). IR (CCl_4): 2 982 m (ν_{as} CH_3); 2 938 w (ν_{as} CH_2 ester); 2 906 w (ν_s CH_3); 2 873 w (ν_s CH_2 ester); 1 733 vs (ν C=O); 1497 w (ν ring); 1 476 w, 1 464 w,

1 457 w, 1 446 w (δ_{as} CH_3 + CH_3 ester); 1 390 w (β_s CH_2 ester); 1 378 w (δ_s CH_3); 1 366 w (δ_s CH_3 ester); 1 298 w, 1 283 m, 1 243 s, 1 188 m, 1 109 s, 1 026 m, 938 w, 908 w, 861 w.

Hexaethyl benzene-1,2,3,4,5,6-hexakis[α-(ethoxycarbonyl)-α-ethylpropanoate] (**4b**). Prepared from hexamalonate **3b** (1.11 g, 1 mmol), sodium hydride/oil suspension (0.65 g, 16 mmol) and ethyl iodide (1.87 g, 12 mmol) in dimethyl sulfoxide (23 ml). The crude product was crystallized twice from ethanol and subsequently from ether–petroleum ether, m.p. 224–225 °C, yield 1.11 g (87%). For $C_{66}H_{102}O_{24}$ (1 279.5) calculated: 61.95% C, 8.04% H; found: 61.59% C, 8.12% H. MS (FAB, DS, $CHCl_3$), *m/z* (rel.%): 1 302 [$(M + Na)^+$, 10], 1 280 [$(M + H)^+$, 9], 1 252 (8), 1 200 (5), 1 128 (6), 1 092 (100), 1 064 (47), 1 018 (14), 988 (11), 905 (19), 875 (13). ^{1}H NMR ($CDCl_3$): 4.33–4.09 m, 24 H (12 × OC**H**$_2$); 3.59 s, 12 H (6 × C**H**$_2$); 1.38 q, $^3J_{HH}$ = 7.3, 12 H (6 × C**H**$_2$CH$_3$); 1.25 t, $^3J_{HH}$ = 7, 36 H (12 × OCH$_2$C**H**$_3$); 0.82 t, $^3J_{HH}$ = 7.3, 18 H (6 × CH$_2$C**H**$_3$). IR (CCl_4): 2 981 m (ν_{as} CH_3); 2 939 m (ν_{as} CH_2 ester); 2 905 w (ν_s CH_3); 2 883 w (ν_s CH_2); 1 728 vs (νC=O); 1 493 w (ν ring); 1 477 w, 1 464 m, 1 445 m (δ_{as} CH_3); 1 390 w (β_s CH_2 ester); 1 382 w, 1 367 m (δ_s CH_3); 1 302 m, 1 257 s, 1 232 s, 1 188 s, 1 161 m, 1 114 s, 1 096 m, 976 w, 922 w, 861 w.

Hexaethyl benzene-1,2,3,4,5,6-hexakis[α-butyl-α-(ethoxycarbonyl)propanoate] (**4c**). Prepared from hexamalonate **3b** (4.44 g, 4 mmol), sodium hydride/oil suspension (1.46 g, 36 mmol) and butyl iodide (8.83 g, 48 mmol) in dimethyl sulfoxide (64 ml). The crude product was crystallized twice from ethanol and subsequently from ether–petroleum ether, m.p. 223–225 °C, yield 4.44 g (77%). For $C_{78}H_{126}O_{24}$ (1 447.8) calculated: 64.71% C, 8.77% H; found: 65.07% C, 8.88% H. MS (FAB, DTT/DTE, $CHCl_3$), *m/z* (rel.%): 1 470 [$(M + Na)^+$, 8], 1448 [$(M + H)^+$, 7], 1 288 (7), 1 260 (37), 1 232 (100), 1 204 (30), 1 176 (54), 1 018 (20). ^{1}H NMR ($CDCl_3$): 4.27–4.11 m, 24 H (12 × OC**H**$_2$); 3.57 s, 12 H (6 × C**H**$_2$); 1.42–1.30 m, 36 H (18 × C**H**$_2$); 1.26 t, $^3J_{HH}$ = 7, 36 H (12 × OCH$_2$C**H**$_3$); 0.82 br t, 18 H (6 × C**H**$_3$). IR (CCl_4): 2 979 m (ν_{as} CH_3 ester); 2 959 s (ν_{as} CH_3 butyl); 2 933 m (ν_{as} CH_2 butyl); 2 905 w (ν_s CH_3); 2 872 m (ν_s CH_2 butyl); 1 730 vs (ν C=O); 1 467 m, 1 457 m, 1 445 m (δ_{as} CH_3); 1 390 w (β_s CH_2 ester); 1 377 w (δ_s CH_3 butyl); 1 367 m (δ_s CH_3 ester); 1 301 m, 1 273 s, 1 238 s, 1 205 s, 1 187 s, 1 158 m, 1 122 m, 1 097 m, 1 042 m, 943 w, 861 w.

Hexaethyl benzene-1,2,3,4,5,6-hexakis[α-benzyl-α-(ethoxycarbonyl)propanoate] (**4d**). Prepared from hexamalonate **3b** (1.11 g, 1 mmol), sodium hydride/oil suspension (410 mg, 10 mmol) and benzyl bromide (1.71 g, 10 mmol) in dimethyl sulfoxide (30 ml). The crude product was crystallized from toluene and subsequently from chloroform–ethanol, m.p. 297–300 °C, yield 1.01 g (61%). For $C_{96}H_{114}O_{24}$ (1 652.0) calculated: 69.80% C, 6.96% H; found: 69.60% C, 6.56% H. MS (FAB, DS, $CHCl_3$ + TFA), *m/z* (rel.%): 1 674 [$(M + Na)^+$, 68], 1 652 [$(M + H)^+$, 65], 1 402 (100). ^{1}H NMR ($CDCl_3$): 6.98–6.81 m, 30 H (Ar-**H**); 4.10–3.90 m, 24 H (6 × OC**H**$_2$ + 6 × C**H**$_2$ alkyl); 2.66 s, 12 H (6 × C**H**$_2$); 0.97 t, $^3J_{HH}$ = 7, 36 H (12 × CH_3). IR (KBr): 3 089 w, 3 062 w, 3 030 w (ν CH benzyl); 2 981 m (ν_{as} CH_3); 2 939 w (ν_{as} CH_2 ester); 2 904 w (ν_s CH_3); 2 873 w (ν_s CH_2); 1 745 s, 1 722 vs (ν C=O); 1 604 w, 1 496 m, 1 455 w (ν ring); 1 474 w, 1 445 w (δ_{as} CH_3); 1 435 w (β_s CH_2); 1 389 w (β_s CH_2 ester); 1 367 m (δ_s CH_3); 1 344 w, 1 322 m (γ_s CH_2); 1 297 w, 1 250 vs, 1 188 s, 1 155 m, 1 113 w, 1 097 m, 1 085 s, 1 053 m, 1 021 w, 891 w, 862 w, 740 m, 699 m.

Hexaethyl benzene-1,2,3,4,5,6-hexakis[α-(ethoxycarbonyl)-α-octylpropanoate] (**4e**). Prepared from hexamalonate **3b** (1.11 g, 1 mmol), sodium hydride/oil suspension (488 mg, 12 mmol) and octyl iodide (3.34 g, 14 mmol) in dimethyl sulfoxide (19 ml). The product was obtained as a thick oil, yield 1.78 g (100%). For $C_{102}H_{174}O_{24}$ (1 784.5) calculated: 68.65% C, 9.83% H; found: 68.81% C, 10.25% H. MS (FAB, DS, $CHCl_3$), *m/z* (rel.%): 1 784 [$(M + H)^+$, 5], 1 682 (8), 1 598 (32), 1 512 (100), 1 400 (11), 1 334 (10), 1 242 (12), 1 211 (34), 1 061 (28). ^{1}H NMR

($CDCl_3$): 4.28–4.12 m, 24 H (12 × OCH_2); 3.56 br s, 12 H (6 × CH_2); 1.29–1.19 m, 120 H (12 × OCH_2CH_3 + 42 × CH_2); 0.84 br t, $^3J_{HH}$ = 6.5, 18 H (6 × CH_3). IR (CCl_4): 2 978 m (ν_{as} CH_3 ester); 2 957 s (ν_{as} CH_3 octyl); 2 928 s (ν_{as} CH_2 octyl); 2 872 m (ν_s CH_2 ester); 2 856 m (ν_s CH_2 octyl); 1 729 vs (ν C=O); 1 466 m, 1 445 w (δ_{as} CH_3); 1 390 w (β_s CH_2 ester); 1 378 w (δ_s CH_3 octyl); 1 367 m (δ_s CH_3 ester); 1 300 m, 1 286 m, 1 230 s, 1 191 m, 1 177 m, 1 133 m, 1 097 m, 1 073 w, 1 047 w, 1 031 m, 861 w.

Hexaethyl benzene-1,2,3,4,5,6-hexakis[α-bromo-α-(ethoxycarbonyl)propanoate] (**4f**). Bromine (9.59 g, 60 mmol) was added dropwise to a solution of hexamalonate **3b** (5.56 g, 5 mmol) and dibenzoyl peroxide (100 mg) in tetrachloromethane (30 ml). The mixture was kept under reflux for 8 h with IR lamp irradiation and the volatiles were evaporated. The residue was dissolved in chloroform, washed successively with aqueous solutions of sodium dithionite, sodium hydrogencarbonate and water. The organic extract was dried (anhydrous $MgSO_4$) and evaporated. The solid residue was triturated with ethanol, filtered off and crystallized twice from butan-1-ol, m.p. 231–232 °C, yield 6.73 g (85%). For $C_{54}H_{72}Br_6O_{24}$ (1 584.6) calculated: 40.93% C, 4.54% H, 30.26% Br; found: 41.22% C, 4.54% H, 30.21% Br. MS (FAB, DS, $CHCl_3$), *m/z* (rel.%): 1 605 [$(M + Na)^+$, 45], 1 585 [$(M + H)^+$, 36], 1 503 (55), 1 457 (70), 1 425 (100), 1 379 (96), 1 347 (100), 1 299 (68), 1 265 (91), 1 219 (65), 1 185 (85), 1 107 (70), 1 067 (87). ^{1}H NMR ($CDCl_3$): 4.31 q, $^3J_{HH}$ = 7, 24 H (12 × OCH_2); 4.05 s, 12 H (6 × CH_2); 1.28 t, $^3J_{HH}$ = 7, 36 H (12 × OCH_2CH_3). IR (CCl_4): 2 982 w (ν_{as} CH_3); 2 935 w (ν_{as} CH_2); 2 908 w (ν_s CH_3); 2 872 w (ν_s CH_2); 1 764 m, sh, 1 741 vs (ν C=O); 1 490 w (ν ring); 1 476 w, sh, 1 466 w, 1 445 w (δ_{as} CH_3); 1 427 w (β_s CH_2 benzyl); 1 392 w (β_s CH_2 ester); 1 368 w (δ_s CH_3); 1 315 w (γ_s CH_2 benzyl); 1 300 w, 1 236 s, 1 178 m, 1 115 w, 1 095 w, 1 059 w, 1 020 w, 965 w, 910 w, 859 w.

Hexaethyl-1,2,3,4,5,6-benzenehexakis(α-azido-α-ethoxycarbonylpropanoate) (**4g**). Hexamalonate **3b** (3.33 g, 3 mmol) was dissolved in dimethyl sulfoxide (57 ml) and stirred for 30 min with sodium hydride prepared from the oil suspension (1.46 g, 36 mmol). To the resulting solution tosyl azide (8.28 g, 42 mmol) in dimethyl sulfoxide (10 ml) was dropwise added under continuous stirring. The reaction mixture was heated at 50 °C for 4–5 h, poured into water (290 ml) and the product was precipitated by addition of ethanol. Then it was washed with water and petroleum ether and crystallized twice from ethanol and subsequently from acetone, m.p. 193–195 °C, yield 1.54 g (38%). For $C_{54}H_{72}N_{18}O_{24}$ (1 357.3) calculated: 47.79% C, 5.35% H, 18.58% N; found: 47.69% C, 5.31% H, 18.48% N. MS (FAB, DS, $CHCl_3$), *m/z* (rel.%): 1 380 [$(M + Na)^+$, 11], 1 330 (15), 1 288 (27), 1 128 (54), 1 100 (56), 1 087 (100), 1 059 (70), 1 046 (47), 1 018 (33), 987 (32), 817 (24), 758 (31), 672 (22), 599 (29), 526 (38), 451 (41). ^{1}H NMR ($CDCl_3$): 4.38–4.23 m, 24 H (12 × OCH_2); 3.66 br s, 12 H (6 × CH_2); 1.32 t, $^3J_{HH}$ = 7, 36 H (12 × OCH_2CH_3). IR (CCl_4): 2 983 w (ν_{as} CH_3); 2 938 w (ν_{as} CH_2); 2 908 w (ν_s CH_3); 2 873 w (ν_s CH_2); 2 126 s (ν_{as} $-N_3$); 1 750 vs, 1 735 m, sh (ν C=O); 1 493 w (ν ring); 1 476 w, sh, 1 466 w, 1 456 w, 1 446 w (δ_{as} CH_3); 1 429 w (β_s CH_2 benzyl); 1 393 w (β_s CH_2 ester); 1 369 w (δ_s CH_3); 1 331 w (γ_s CH_2 benzyl); 1 282 m (ν_s $-N_3$); 1 297 w, 1 226 s, 1 216 s, 1 188 m, 1 115 w, sh, 1 097 w, 1 059 m, 1 039 w, 1 016 w, 924 w, 860 w, 680 w (β N_3).

X-Ray Structure Analysis

Single crystals were obtained by the following procedures: vapour diffusion of petroleum ether into a solution in ethyl acetate (compounds **3b** and **4a**), a slow evaporation of a solution in acetone–heptane (compound **4b**), a slow cooling of a solution in toluene–petroleum ether (compound **4c**), vapour diffusion of pentane into a solution in diethyl ether (com-

TABLE II
X-Ray crystallographic data[a]

Compound	**3b**	**4a**	**4b**[b]	**4c**	**4f**	**4g**[e]
Formula	$C_{54}H_{78}O_{24}$	$C_{60}H_{90}O_{24}$	$C_{66}H_{102}O_{24}$	$C_{78}H_{126}O_{24}$	$C_{54}H_{72}Br_6O_{24}$	$C_{54}H_{72}N_{18}O_{24}$
M.w.	1 111.19	1 195.36	1 279.52	1 447.84	1 584.56	1 357.26
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	trigonal	monoclinic
Space group [No.]	*C2/c*[15]	$P2_1/c$[14]	$P\bar{1}$[2]	$P2_1/n$[14]	$R\bar{3}m$[166]	*C2/c*[15]
a, Å	21.712(2)	14.070(2)	12.698(3)	14.284(4)	21.700(5)	44.186(4)
b, Å	13.527(2)	21.052(2)	13.543(3)	16.953(6)		19.997(2)
c, Å	20.954(3)	11.836(1)	23.181(7)	17.250(3)	12.604(5)	15.259(1)
α, °			72.89(2)			
β, °	97.439(9)	110.083(9)	74.06(2)	98.93(2)		106.608(8)
γ, °			65.13(2)		120.000(5)	
Z	4	2	2	2	3	8
V, Å^3	6 102(1)	3 297.7(6)	3 404(2)	4 127(2)	5 140(3)	12 920(2)
F(000)	2 376	1 284	1 380	1 572	2 394	5 712
ρ_{calc}, g cm^{-3}	1.209	1.206	1.248	1.165	1.536	1.396
Crystal size, mm	0.4 × 0.5 × 0.6	0.2 × 0.4 × 0.5	0.3 × 0.4 × 0.4	0.4 × 0.6 × 0.9	0.5 × 0.5 × 0.8	0.2 × 0.2 × 0.2
Crystal shape	prism	plate	prism	parallelepiped	prism	cuboid
μ, mm^{-1}	0.095	0.093	0.094	0.085	3.586[d]	0.111
θ_{max}, °	25	25	22	24	25	25
Range of *h,k,l*	0→17, 0→16, –24→24	–16→15,–25→0, 0→13	0→13, –12→14, –22→24	–16→16, 0→19, 0→19	–25→22, 0→25, 0→15	–46→47, –22→23, –17→17

TABLE II
(*Continued*)

Compound	**3b**	**4a**	**4b**[b]	**4c**	**4f**	**4g**[e]
Decay of 3 standard reflections (monitored every 1 h)	2.8	2.6	4.5	4	9	1
Measured reflections	10 173	5 193	8 356	6 582	3 238	15 998
Independent reflections (R_{int})	4 570 (0.012)	5 193	8 356	6 352 (0.029)	1 098 (0.067)	9 226 (0.068)
Observed reflections $I > 2\sigma(I)$	3 009	2 063	5 021	4 340	782	8 917
No. of parameters	352	379	830[c]	460	115	877
R; R_w, %	6.49; 17.02	7.38; 18.42	8.14; 21.54	5.01; 13.08	5.65; 14.89	7.95; 20.70
GOF	1.037	1.009	1.073	1.050	1.089	1.088
Residual electron density, e Å^{-3}	0.40; –0.32	0.51; –0.27	0.86; –0.45	0.56; –0.29	1.01; –0.32	0.83; –0.84

[a] Details in common: colourless crystal, CAD 4 diffractometer, MoKα (λ = 0.71069Å), 293(2) K, θ–2θ scan; direct methods (SHELXS86)[18], full-matrix least-squares on F^2 (SHELXL93)[19], hydrogen atoms in calculated positions (SHELXL93) with temperature factor 1.5 of those of their bonding partners; [b] at 150 K; [c] one multiply disordered ethoxy group (see text) refined isotropically, their hydrogen atoms ignored; [d] numerical absorption correction, T_{min} = 0.109, T_{max} = 0.242; [e] synchrotron radiation source of HXRD beamline in Electra (Sincrotrone Trieste SpA, Padricano, Trieste, Italy), λ = 0.8 Å, θ_{max} = 28.15°, MAR345 image plate detector (30 cm in diameter, giving 0.85 Å resolution at edge), rotating crystal, 100 K, ψ-range 190°, ψ-step 5°, data reduction using HKL (ref.[20]).

pound **4f**), and a slow evaporation of a solution in aqueous ethanol (compound **4g**). The crystal data and common measurement and refinement details are summarized in Table II. Perspective views of the molecules with atom labelling are in Figs 1–6.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers: **3b**, CCDC-140428; **4a**, CCDC-140429; **4b**, CCDC-140430; **4c**, CCDC-140431; **4f**, CCDC-140432; **4g**, CCDC-140433. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

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