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Stereochemical Studies of Oligomers. V. * 2,4-Pentanediyil Dibenzoate, C₁₉H₂₀O₄

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Abstract. $M_r = 312.4$, $P2_12_12_1$, $a = 10.976$ (2), $b = 11.706$ (2), $c = 13.013$ (2) Å, $V = 1672.0$ (5) Å³, $Z = 4$, $D_x = 1.24$ g cm⁻³, Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 6.66$ cm⁻¹, $F(000) = 664$, $T = 298$ K, $R = 0.034$ for 894 observed reflections. The conformation of the chain produces a rotation of one aromatic ring with respect to the other and the molecule assumes an *endo* conformation. The introduction of pendant methyl groups on the aliphatic chain radically changes the molecular conformation compared with those found in the analogous unmethylated oligomer and in its related polymer.

Introduction. The crystal analysis results of oligomers in which the conformation of the aliphatic chain seems greatly influenced by pendant methyl groups has already been reported (Bocelli & Grenier-Loustalot, 1982b, 1983). From these studies and from those obtained spectroscopically rose the necessity to have more data to clarify the role of the pendant methyls in the conformational change and to try to form a rationalization of these variations. Consequently we have synthesized a new series of this type of oligomer and the results of the crystal analysis of the first of these is reported in this paper.

Experimental. Crystals grown from methanol solution, colorless prism, $0.21 \times 0.33 \times 0.49$ mm, accurate cell constants determined by least squares from 20 reflections automatically centered on a Siemens diffractometer, reflection centering performed by *CTDIF* routine (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979); 1854 reflections ($2 < \theta < 70^\circ$) collected with Ni-filtered Cu $K\alpha$ radiation, 895 considered as observed

[$I > 2\sigma(I)$] used for subsequent analysis, scan speed ($6-24$ s deg⁻¹) determined from the intensity of a 'flash' (1 s), scans taken from Δ_0 below θ to Δ_1 above ($\Delta_0 = 0.55^\circ$; $\Delta_1 = \{0.55 + [(\lambda\alpha_1 - \lambda\alpha_2)/\lambda]\tan\theta\}^\circ$), integrated intensities obtained by a modification of the Lehmann & Larsen (1974) procedure using a program written by Belletti *et al.* (1979), 1 standard reflection monitored every 50 measurements, statistical fluctuations in intensity corrected during data processing with Lp corrections, absorption effects neglected; direct methods with *SHELX* (Sheldrick, 1976), $E's > 1.2$ used, starting set of $E's$ with assigned phases for origin, enantiomorph and multisolution phases chosen manually, position of all heavy atoms found on an E map with best consistency, full-matrix least-squares refinement with anisotropic thermal parameters, all hydrogen atoms found from a difference synthesis and refined isotropically, $R = 0.0338$ ($R_w = 0.0336$); on a final difference synthesis no peaks greater than 0.13 e Å⁻³, $w = [\sigma^2(F_o^2) + 0.027F_o^2]^{-1}$, reflection 200 omitted in the last cycles, scattering factors of *SHELX* used.

All calculations performed on the CDC CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna) with financial support of the University of Parma.

Discussion. The positional parameters are listed in Table 1† and a projection of the molecule with arbitrary numbering is given in Fig. 1. Table 2 lists bond lengths and angles and selected torsion angles.

† Lists of structure factors, anisotropic thermal parameters, coordinates of H atoms with their bond distances, and contacts < 3.5 Å have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38359 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Part IV: Bocelli & Grenier-Loustalot (1982a).

The geometrical parameters of the two aromatic rings, which are planar within experimental error, are normal, the mean C—C and C—H distances and the mean C—C—C and C—C—H angles being 1.381 (4), 1.382 (7), 0.99 (2), 1.00 (2) Å, 119.9 (3), 120.0 (4), 119.8 (13), 119.8 (14)° for the two rings respectively. These rings are quasi-parallel and form a dihedral angle of 10.0 (2)°.

Table 1. Fractional atomic coordinates ($\times 10^4$) and isotropic B_{eq} (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^*
O(1)	805 (3)	3619 (3)	6898 (3)	4.87 (4)
O(2)	-1206 (3)	3963 (3)	6800 (3)	5.86 (5)
O(3)	504 (3)	5409 (3)	5349 (3)	5.25 (5)
O(4)	-1272 (4)	6229 (4)	4933 (4)	8.70 (6)
C(1)	-356 (4)	2432 (4)	5838 (3)	3.71 (3)
C(2)	-1405 (5)	2272 (5)	5256 (4)	4.34 (6)
C(3)	-1449 (6)	1420 (5)	4541 (5)	5.42 (5)
C(4)	-471 (5)	702 (5)	4391 (5)	5.73 (6)
C(5)	560 (5)	841 (5)	4982 (5)	5.45 (5)
C(6)	629 (5)	1700 (4)	5704 (4)	4.43 (4)
C(7)	-324 (5)	3412 (4)	6551 (4)	4.24 (4)
C(8)	971 (5)	4591 (5)	7596 (4)	5.02 (5)
C(9)	1881 (8)	4144 (8)	8385 (6)	7.11 (6)
C(10)	1469 (5)	5602 (5)	6990 (5)	5.52 (5)
C(11)	642 (6)	6185 (5)	6227 (5)	5.62 (6)
C(12)	1145 (9)	7313 (7)	5844 (7)	8.15 (7)
C(13)	-479 (6)	5531 (5)	4757 (5)	5.47 (6)
C(14)	-495 (5)	4741 (5)	3871 (4)	4.87 (5)
C(15)	423 (5)	3940 (5)	3705 (5)	5.05 (5)
C(16)	357 (6)	3194 (5)	2895 (5)	5.88 (5)
C(17)	-635 (7)	3239 (7)	2247 (5)	6.76 (6)
C(18)	-1522 (8)	4030 (8)	2375 (6)	7.44 (6)
C(19)	-1481 (6)	4778 (6)	3184 (6)	6.25 (7)

* According to Hamilton (1959).

Table 2. Bond distances (Å), bond angles (°) and selected torsion angles (°)

O(1)—C(7)	1.341 (6)	C(1)—C(7)	1.476 (7)	C(11)—C(12)	1.516 (11)
O(1)—C(8)	1.467 (7)	C(2)—C(3)	1.365 (8)	C(13)—C(14)	1.478 (8)
O(2)—C(7)	1.208 (6)	C(3)—C(4)	1.377 (9)	C(14)—C(15)	1.393 (8)
O(3)—C(11)	1.468 (7)	C(4)—C(5)	1.378 (8)	C(14)—C(19)	1.404 (9)
O(3)—C(13)	1.333 (7)	C(5)—C(6)	1.378 (8)	C(15)—C(16)	1.371 (9)
O(4)—C(13)	1.216 (8)	C(8)—C(9)	1.525 (10)	C(16)—C(17)	1.378 (10)
C(1)—C(2)	1.391 (7)	C(8)—C(10)	1.524 (8)	C(17)—C(18)	1.354 (12)
C(1)—C(6)	1.391 (7)	C(10)—C(11)	1.509 (9)	C(18)—C(19)	1.370 (11)
C(7)—O(1)—C(8)	117.6 (4)	C(8)—C(10)—C(11)	118.4 (5)		
C(11)—O(3)—C(13)	117.8 (4)	O(3)—C(11)—C(12)	107.1 (5)		
C(6)—C(1)—C(7)	122.6 (4)	C(10)—C(11)—C(12)	113.0 (6)		
C(2)—C(1)—C(7)	117.8 (4)	O(3)—C(11)—C(12)	108.7 (6)		
C(2)—C(1)—C(6)	119.5 (4)	O(3)—C(13)—O(4)	122.9 (6)		
C(1)—C(2)—C(3)	119.9 (5)	O(4)—C(13)—C(14)	124.0 (6)		
C(2)—C(3)—C(4)	121.0 (6)	O(3)—C(13)—C(14)	113.2 (5)		
C(3)—C(4)—C(5)	119.3 (6)	C(13)—C(14)—C(19)	119.1 (5)		
C(4)—C(5)—C(6)	120.8 (5)	C(13)—C(14)—C(15)	122.2 (5)		
C(1)—C(6)—C(5)	119.5 (5)	C(15)—C(14)—C(19)	118.6 (6)		
O(2)—C(7)—C(1)	124.4 (5)	C(14)—C(15)—C(16)	120.7 (5)		
O(1)—C(7)—C(1)	112.0 (4)	C(15)—C(16)—C(17)	119.2 (6)		
O(1)—C(7)—O(2)	123.6 (5)	C(16)—C(17)—C(18)	121.3 (7)		
O(1)—C(8)—C(10)	109.1 (4)	C(17)—C(18)—C(19)	120.5 (8)		
O(1)—C(8)—C(9)	103.4 (5)	C(14)—C(19)—C(18)	119.7 (7)		
C(9)—C(8)—C(10)	112.3 (5)				
C(2)—C(1)—C(7)—O(1)	-166.7 (4)	O(4)—C(13)—C(14)—C(15)	-0.5 (10)		
C(6)—C(1)—C(7)—O(1)	11.0 (7)	O(4)—C(13)—C(14)—C(15)	-179.0 (6)		
C(2)—C(1)—C(7)—O(2)	13.7 (8)	O(3)—C(13)—C(14)—C(19)	180.0 (5)		
C(6)—C(1)—C(7)—O(2)	-168.7 (5)	O(3)—C(13)—C(14)—C(15)	1.5 (8)		
C(1)—C(7)—O(1)—C(8)	-178.6 (4)	C(11)—O(3)—C(13)—C(14)	177.4 (5)		
O(2)—C(7)—O(1)—C(8)	1.8 (7)	C(11)—O(3)—C(13)—O(4)	-2.2 (9)		
C(7)—O(1)—C(8)—C(9)	140.2 (5)	C(12)—C(11)—O(3)—C(13)	80.5 (7)		
C(7)—O(1)—C(8)—C(10)	-100.1 (5)	C(10)—C(11)—O(3)—C(13)	-157.0 (5)		
O(1)—C(8)—C(10)—C(11)	69.8 (6)	C(8)—C(10)—C(11)—O(3)	-72.3 (6)		
O(1)—C(8)—C(10)—C(11)	-176.2 (6)	C(8)—C(10)—C(11)—C(12)	167.9 (6)		

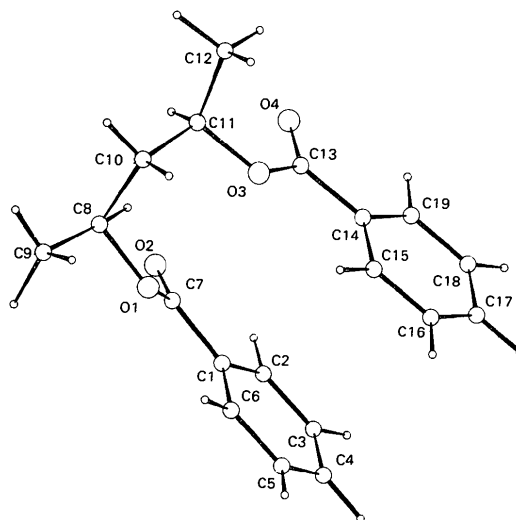


Fig. 1. Projection of the molecule.

The C=O double bond lengths [O(2)—C(7) = 1.208 (6), O(4)—C(13) = 1.216 (8) Å] agree well with the value of 1.215 (5) Å proposed by Sutton (1965); the shorter of these values is counterbalanced by a relative lengthening of the adjacent O(1)—C(7) bond [1.341 (6) Å]. The two C—O single bonds present a pair of different values, two of them being involved in π delocalization with the adjacent C=O bonds.

The Csp^3-Csp^3 distances compare well with the value of 1.526 (2) Å proposed by Lide (1962) while they are shorter if compared with the values indicated by Bonham, Bartell & Kohl (1959) (1.538 Å) or by Sutton (1965) (1.537 Å). It is interesting to observe that the presence of pendant methyl groups greatly reduces, or eliminates in this case, the significant shortening of the —CH₂—CH₂ bonds which was generally found in the *n*-methylene dibenzoates previously studied (Pérez & Brisse, 1975, 1976*a,b*, 1977*a,b*).

The conformation of the molecule as a whole is indicated by the torsion angles of the aliphatic chain which assumes a *gauche-gauche* conformation in its propylenic fragment, the two torsion angles being near to 60° [O(1)—C(8)—C(10)—C(11) = 69.8 (6), C(8)—C(10)—C(11)—O(3) = -72.3 (6)°]. Two of the remaining torsion angles are remarkably different [C(7)—O(1)—C(8)—C(10) = -100.1 (5), C(13)—O(3)—C(11)—C(10) = -157.0 (5)°]. This conformation determines a rotation of one aromatic group with respect to the other and the molecule assumes an *endo* conformation with a quasi-overlapping of the rings along a direction which forms angles of 92.4 (2), 43.5 (2) and 133.4 (2)° with *x*, *y*, *z* axes respectively.

As already observed for a great number of analogous derivatives (Bocelli & Grenier-Loustalot, 1982*c*, 1983 and papers quoted therein), the two carboxylic moieties

are planar and form angles of 12.9 (3) and 1.9 (2)° with the respective mean aromatic ring planes. The first value is larger than the angle of 7.5° measured for ethylene bis(*p*-chlorobenzoate) (Pérez & Brisse, 1975) which is the greatest reported in the literature for these compounds and is very near to that reported for the polyethylene terephthalate (12°) (Daubeny, Bunn & Brown, 1954).

Besides the torsion angles, the conformation of the C(9) and C(12) methyl groups may be described by the angles they form with the O(1), C(8), C(10) and O(3), C(11), C(10) and the O(2), C(7), O(1), C(8) and O(4), C(13), O(3), C(11) mean planes which are 32.4 (5), 143.0 (6), 50.8 (3) and 159.8 (4)°, respectively. Consequently, C(12) is *axial* and C(9) *equatorial* with respect to the chain.

The two carbonylic oxygens are *cis* with respect to the chain.

The crystal packing, which can be seen in Fig. 2, is determined by normal van der Waals interactions.

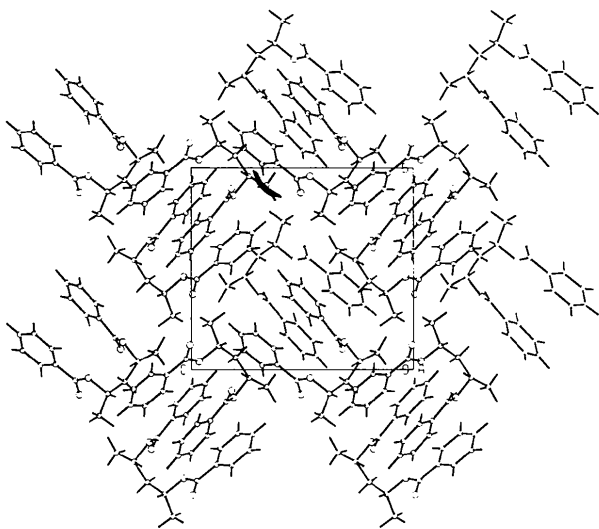


Fig. 2. Packing of the compound along the *x* axis.

The crystal structure determination of the title compound completes the *n*-methylene dibenzoate series (*n* = 2,3,4) for which the structures of oligomers, of di-methylated oligomers and of polymers are now available. Unfortunately, these data are not enough to offer a rationalization of the changes in the chain conformation which seems not univocally influenced by the presence of pendant methyl groups. This fact suggests that more conformational information is needed, and further crystallographic and spectroscopic work in this respect is in progress.

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Benzenehexacarbonitrile at 120 K, C₁₂N₆

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Abstract. $M_r = 228.176$, cubic, $Pa3$, $a = 10.781$ (6) Å, $V = 1253.1$ (1) Å³, $Z = 4$, $D_x = 1.21$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $F(000) = 456$. Final $R =$

0.048 for the 'free-atom model' including 501 independent reflections. The molecule occupies one 4(*a*) position with $\bar{3}$ point symmetry of the space group. All