

**Stereochemical Studies of Oligomers. XIII.* The Structures of 2,5-Hexanediyl
Bis(*p*-chlorobenzoate) and 2,5-Hexanediyl Bis(*m*-chlorobenzoate) (HDP and HDM),
C₂₀H₂₀Cl₂O₄**

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Abstract. $M_r = 395.3$, Ni-filtered Cu K α radiation, $\bar{\lambda} = 1.54178 \text{ \AA}$, room temperature. HDP: triclinic, $P1$, $a = 12.512 (3)$, $b = 12.333 (2)$, $c = 7.166 (2) \text{ \AA}$, $\alpha = 92.81 (2)$, $\beta = 85.84 (2)$, $\gamma = 63.84 (3)^\circ$, $V = 985.8 (9) \text{ \AA}^3$, $Z = 2$, $D_x = 1.33 \text{ g cm}^{-3}$, $\mu = 31.9 \text{ cm}^{-1}$, $F(000) = 412$, $R = 0.065$ for 2608 observed reflections. HDM: triclinic, $P1$, $a = 8.817 (3)$, $b = 8.084 (2)$, $c = 7.341 (2) \text{ \AA}$, $\alpha = 104.35 (3)$, $\beta = 79.06 (4)$, $\gamma = 87.70 (4)^\circ$, $V = 495.6 (3) \text{ \AA}^3$, $Z = 2$, $D_x = 2.65 \text{ g cm}^{-3}$, $\mu = 63.5 \text{ cm}^{-1}$, $F(000) = 412$, $R = 0.065$ for 1637 observed reflections. The conformation of the tetramethylene chain is *gauche-trans-gauche* in HDM while it is relatively far from an all-*trans* arrangement in HDP. In the latter compound the aromatic rings are quasi-parallel [$1.4 (1)^\circ$] to each other and the carboxylic groups are tilted by $0.4 (2)$ and $2.3 (2)^\circ$. In HDM the rings are parallel for symmetry requirements and subtend an angle of $6.0 (1)^\circ$ with respect to their carboxylic moiety.

Introduction. The information gained by X-ray diffraction on oligomers, which are the object of intensive research in progress in our laboratories, is of great importance in energy calculations and is also helpful in spectroscopic studies. Besides, as previously pointed out for many biopolymers and some polyesters (Brisse, Marchessault & Pérez, 1980), the knowledge of the single-crystal structures of these 'model compounds' may permit a correct polymer structure to be obtained. The results of the crystal analyses here reported constitute a new step in this field of research.

Experimental. For both compounds: Siemens AED single-crystal diffractometer, General Automation Jumbo 220 computer, speed range 6–24 s deg⁻¹, scan range from Δ_0 below θ to Δ_1 above ($\Delta_0 = 0.55^\circ$, $\Delta_1 = \{0.55 + [(\lambda_{\alpha_1} - \lambda_{\alpha_2})/\bar{\lambda}] \tan \theta\}^\circ$), intensities collected with a modified version (Belletti, Ugozzoli, Cantoni &

Pasquinelli, 1979) of the Lehmann & Larsen (1974) procedure, 1 reference reflection collected every 50 measurements, Lp correction, absorption ignored.

HDP: colourless prism grown in ethanol, $0.7 \times 0.9 \times 1.1$ mm, symmetry and cell parameters by least squares of angular values for 29 reflections automatically centred on diffractometer, $2 \leq \theta \leq 65^\circ$, $-14 \leq h \leq 14$, $-13 \leq k \leq 14$, $0 \leq l \leq 8$, check reflection with only statistical variation in intensity, 3312 unique reflections, 2608 with $I \geq 3\sigma(I)$ observed, direct methods, refinement by block-matrix least squares with *SHELX* (Sheldrick, 1976), H (from ΔF map) isotropic, rest anisotropic, final R and R_w , 0.065 and 0.081, respectively, $w = 1.0/(\sigma^2 F + 0.037 F^2)$, minimization function $\sum w(\Delta F)^2$, final ΔF map with no residual peaks $> 0.26 \text{ e \AA}^{-3}$.

HDM: pyramid-shaped fragment cut from larger one recrystallized from ethanol, $0.2 \times 0.5 \times 0.9$ mm, cell parameters from 26 reflections, no significant variation in check reflection, 1817 unique reflections collected, 1637 observed [$I \geq 2\sigma(I)$], $2 \leq \theta \leq 70^\circ$, $-10 \leq h \leq 10$, $-9 \leq k \leq 9$, $0 \leq l \leq 8$, direct methods, refinement by anisotropic full-matrix least squares with *SHELX*, H (from ΔF map) isotropic, final $R = 0.065$, $R_w = 0.083$, $w = 1.0/(\sigma^2 F + 0.0032 F^2)$, $\sum w(\Delta F)^2$ minimized, $\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$, $(\Delta/\sigma)_{\max} = 0.33$. Scattering factors from *SHELX*, all calculations on a Gould SEL 32/77 computer.†

Discussion. Table 1 gives the atomic coordinates and Table 2 bond lengths and angles and selected torsion angles. Views of the molecules are shown in Figs. 1 and 2.

† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39308 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Part XII: Bocelli & Grenier-Loustalot (1984b).

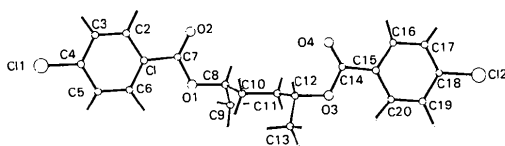


Fig. 1. Projection of HDP.

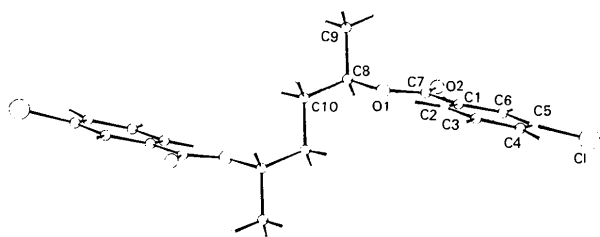


Fig. 2. Projection of HDM.

Table 1. Fractional atomic coordinates ($\times 10^4$) with B_{eq} values (\AA^2)

	x	y	z	B_{eq}^*
HDP				
Cl(1)	1714	8330	9389	7.05
Cl(2)	18529 (1)	129 (1)	5484 (2)	7.88
O(1)	7507 (2)	4971 (2)	6735 (3)	5.30
O(2)	7485 (2)	6793 (2)	6827 (4)	7.11
O(3)	12756 (2)	2133 (2)	8299 (3)	4.89
O(4)	12796 (2)	3936 (2)	8281 (4)	6.19
C(1)	5670 (2)	6658 (2)	7603 (4)	4.28
C(2)	5014 (3)	7906 (3)	7963 (5)	4.91
C(3)	3800 (3)	8416 (3)	8485 (5)	5.16
C(4)	3245 (2)	7673 (3)	8674 (5)	4.95
C(5)	3872 (3)	6443 (3)	8357 (6)	6.12
C(6)	5096 (3)	5932 (3)	7821 (6)	5.55
C(7)	6974 (2)	6164 (2)	7006 (4)	4.48
C(8)	8798 (3)	4362 (3)	6112 (5)	5.30
C(9)	8970 (4)	3571 (5)	4390 (7)	7.11
C(10)	9430 (2)	3748 (3)	7747 (5)	4.28
C(11)	10788 (3)	3117 (3)	7265 (5)	4.91
C(12)	11468 (2)	2719 (3)	8963 (5)	5.16
C(13)	11254 (3)	1779 (4)	9948 (6)	4.95
C(14)	13295 (2)	2855 (2)	7988 (4)	6.12
C(15)	14583 (2)	2133 (2)	7322 (4)	5.55
C(16)	15269 (3)	2767 (3)	7022 (5)	4.48
C(17)	16474 (3)	2139 (3)	6428 (5)	7.88
C(18)	17011 (3)	914 (4)	6172 (5)	4.89
C(19)	16357 (3)	246 (3)	6435 (5)	6.19
C(20)	15146 (3)	881 (3)	7008 (4)	5.12
HDM				
Cl	930	4884	7162	8.66
O(1)	7402 (2)	1334 (2)	7127 (2)	3.80
O(2)	5169 (2)	77 (2)	7274 (2)	4.31
C(1)	5134 (2)	3047 (2)	7359 (2)	3.18
C(2)	5966 (3)	4485 (3)	7485 (3)	3.98
C(3)	5217 (4)	6044 (3)	7553 (3)	4.90
C(4)	3676 (3)	6181 (3)	7469 (3)	4.97
C(5)	2862 (3)	4747 (3)	7351 (3)	4.69
C(6)	3573 (2)	3169 (3)	7316 (3)	3.77
C(7)	5877 (2)	1326 (2)	7249 (3)	3.17
C(8)	8285 (2)	-291 (3)	6975 (3)	3.68
C(9)	8160 (3)	562 (4)	8971 (3)	4.91
C(10)	9933 (2)	-130 (3)	6009 (3)	4.20

* According to Hamilton (1959).

Table 2. Interatomic distances (\AA), valence angles ($^\circ$) and selected torsion angles ($^\circ$)

	HDP	HDM	HDP	
Cl(1)-C(4)	1.743 (5)		Cl(2)-C(18)	1.727 (6)
Cl-C(5)		1.737 (3)		
O(1)-C(7)	1.317 (5)	1.331 (3)	O(3)-C(14)	1.351 (5)
O(1)-C(8)	1.472 (6)	1.469 (3)	O(3)-C(12)	1.474 (5)
O(2)-C(7)	1.209 (5)	1.210 (3)	O(4)-C(14)	1.196 (5)
C(1)-C(2)	1.388 (6)	1.392 (3)	C(15)-C(16)	1.406 (6)
C(1)-C(6)	1.381 (6)	1.383 (3)	C(15)-C(20)	1.384 (6)
C(1)-C(7)	1.488 (5)	1.491 (3)	C(14)-C(15)	1.483 (6)
C(2)-C(3)	1.377 (6)	1.384 (4)	C(16)-C(17)	1.378 (6)
C(3)-C(4)	1.378 (6)	1.373 (5)	C(17)-C(18)	1.352 (7)
C(4)-C(5)	1.364 (6)	1.381 (4)	C(18)-C(19)	1.404 (7)
C(5)-C(6)	1.389 (6)	1.391 (5)	C(19)-C(20)	1.382 (6)
C(8)-C(9)	1.476 (7)	1.519 (4)	C(12)-C(13)	1.497 (7)
C(8)-C(10)	1.505 (6)	1.517 (3)	C(11)-C(12)	1.512 (6)
C(10)-C(11)	1.528 (6)			
C(10)-C(10')		1.513 (3)		
C(7)-O(1)-C(8)	118.2 (8)	117.7 (2)	C(8)-C(10)-C(11)	111.6 (4)
C(12)-O(3)-C(14)	117.9 (6)		C(10)-C(11)-C(12)	113.3 (4)
C(6)-C(1)-C(7)	123.0 (7)	117.4 (2)	O(3)-C(12)-C(11)	107.5 (4)
C(2)-C(1)-C(7)	117.8 (7)	122.0 (3)	C(11)-C(12)-C(13)	114.2 (6)
C(2)-C(1)-C(6)	119.2 (7)	120.6 (2)	O(3)-C(12)-C(13)	105.2 (6)
C(1)-C(2)-C(3)	120.4 (8)	119.3 (3)	O(3)-C(14)-O(4)	123.7 (7)
C(2)-C(3)-C(4)	119.3 (7)	120.9 (3)	O(4)-C(14)-C(15)	124.9 (8)
Cl(1)-C(4)-C(3)	118.8 (6)		O(3)-C(14)-C(15)	111.4 (6)
C(3)-C(4)-C(5)	121.5 (9)	119.3 (3)	C(14)-C(15)-C(20)	124.0 (8)
Cl(1)-C(4)-C(5)	119.8 (8)		C(14)-C(15)-C(16)	117.5 (6)
Cl-C(5)-C(4)		119.8 (2)	C(16)-C(15)-C(20)	118.5 (7)
C(4)-C(5)-C(6)	118.9 (3)	118.9 (3)	C(15)-C(16)-C(17)	119.9 (7)
C(1)-C(6)-C(5)	120.6 (7)	118.6 (3)	C(16)-C(17)-C(18)	120.6 (9)
O(2)-C(7)-C(1)	123.4 (7)	123.7 (3)	Cl(2)-C(18)-C(17)	120.4 (8)
O(1)-C(7)-C(1)	112.5 (7)	112.0 (2)	C(17)-C(18)-C(19)	121.4 (8)
O(1)-C(7)-O(2)	124.1 (7)	124.4 (2)	Cl(2)-C(18)-C(19)	118.2 (6)
O(1)-C(8)-C(10)	107.3 (4)	105.7 (2)	C(18)-C(19)-C(20)	117.8 (7)
O(1)-C(8)-C(9)	107.3 (8)	109.0 (2)	C(15)-C(20)-C(19)	121.8 (8)
C(9)-C(8)-C(10)	116.5 (5)	113.2 (2)		
C(8)-C(10)-C(10')		113.4 (2)		

Table 2 (cont.)

	HDP	HDM	HDP	HDM	HDP
C(2)-C(1)-C(7)-O(1)	178.9 (8)	-5.2 (3)	C(7)-O(1)-C(8)-C(10)	108.2 (9)	155.8 (2)
C(2)-C(1)-C(7)-O(2)	0.2 (13)	174.6 (3)	O(1)-C(8)-C(10)-C(11)	-178.2 (7)	
C(6)-C(1)-C(7)-O(1)	-0.7 (12)	174.3 (2)	O(1)-C(8)-C(10)-C(10')		-61.1 (3)
C(6)-C(1)-C(7)-O(2)	-179.4 (9)	-5.9 (4)	C(9)-C(8)-C(10)-C(11)	61.5 (10)	
C(1)-C(7)-O(1)-C(8)	179.1 (7)	-179.0 (2)	C(9)-C(8)-C(10)-C(10')		176.6 (2)
O(2)-C(7)-O(1)-C(8)	-2.2 (14)	1.3 (4)	C(8)-C(10)-C(11)-C(12)	167.8 (7)	
C(7)-O(1)-C(8)-C(9)	-125.8 (9)	-82.2 (3)	C(8)-C(10)-C(10')-C(8')		180.0 (2)
C(10)-C(11)-C(12)-O(3)					-179.8 (7)
C(10)-C(11)-C(12)-C(13)					63.9 (10)
C(11)-C(12)-O(3)-C(14)					81.8 (10)
C(13)-C(12)-O(3)-C(14)					-156.1 (8)
C(12)-O(3)-C(14)-C(15)					-179.8 (7)
C(12)-O(3)-C(14)-O(4)					2.6 (14)
O(3)-C(14)-C(15)-C(16)					-177.2 (8)
O(4)-C(14)-C(15)-C(16)					0.3 (14)
O(3)-C(14)-C(15)-C(20)					1.8 (12)
O(4)-C(14)-C(15)-C(20)					179.4 (9)

The title compounds differ from one compound already analysed (Bocelli & Grenier-Loustalot, 1982*a*) only by the two chlorine atoms on the rings, but the conformations of the tetramethylene segments are strikingly different. In fact a *gauche-trans-gauche* conformation characterizes the chains of HDM and the unchlorinated derivative, while HDP shows a significant displacement from an all-*trans* arrangement [C(8)–C(10)–C(11)–C(12) = 167.8 (7)]. The conformation of the rest of the chain of HDP and HDM remains quite similar to that in the unchlorinated derivative, which is in all three cases significantly shifted away from a *trans* arrangement by the conformation around C(7)–O(1)–C(8)–C(10) and C(11)–C(12)–O(3)–C(14). Further differences between the unchlorinated and chlorinated compounds occur in the orientation of the C(9) and C(13) methyl groups which are *trans* each to other and axial with respect to the chain in the first case and in HDM. In HDP they lie on the same side with respect to the C(8)–C(10)–C(11)–C(12) sequence [1.00 (8) and 1.05 (9) Å out of plane]. Moreover, in HDP, the dihedral angles [43.5 (7) and 41.2 (7)°] formed by the bond direction with the normal to the least-squares plane force the methyls to occupy a position intermediate between axial and equatorial.

It may be interesting to compare the chain conformation of the present structures with those of 1,4-butanediyl dibenzoate (Bocelli & Grenier-Loustalot, 1982*b*) and 1,4-butanediyl bis(*p*-chlorobenzoate) (Bocelli & Grenier-Loustalot, 1984*a*) which are *gauche-trans-trans* and all-*trans*, respectively.

These conformational changes of the aliphatic chain reflect on the length (distance between the centre of the rings) of the molecules which is 9.53 (4) Å in the derivative with no substituent, 11.51 (6) Å in that with only the methyls, 13.06 (6) Å in that with only the chlorines and 12.71 (9), 11.54 (2) Å in HDP and HDM, respectively.

The geometry of the benzene rings is normal [1.380 (4), 1.385 (8) and 1.386 (3) Å, 119.9 (4), 119.8 (7) and 120.1 (4)° – average distances and internal angles] and their planes form a dihedral angle

of 1.4 (1)° in HDP and are parallel by geometry requirements in HDM. In agreement with the results of Domenicano, Vaciago & Coulson (1975), Domenicano, Mazzeo & Vaciago (1976), and Domenicano & Murray-Rust (1979), the internal angles at the chlorine atoms are larger than the adjacent ones.

The carboxylic moieties are tilted by 0.4 (2), 2.3 (2) and 6.0 (1)° with respect to their aromatic rings. The angles opposite the C=O bonds show the usual narrowing with respect to the adjacent ones.

The packing of the molecules in the unit cell is determined by van der Waals interactions and no significant intermolecular contacts are observed.

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The Structure of 1,7-Heptanediamine Dihydrobromide at 173 K, C₇H₁₈N₂·2HBr

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Abstract. $M_r = 292.06$, m.p. = 531 K, monoclinic, $P2_1/c$, $a = 4.766$ (5), $b = 16.915$ (10), $c = 14.856$ (14) Å, $\beta = 97.54$ (8)°, $V = 1187.4$ Å³, $Z = 4$,

$D_m = 1.53$, $D_x = 1.593$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 6.55$ mm⁻¹, $F(000) = 584$, $T = 173$ K, final $R = 0.043$ for 1310 observed reflections. The