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4-*n*-Heptylbenzoic Acid

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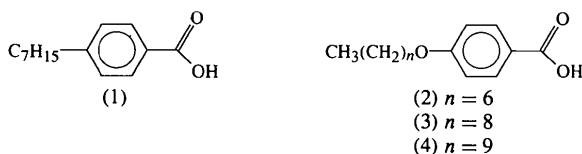
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Abstract

Molecules of 4-*n*-heptylbenzoic acid, C₁₄H₂₀O₂, occur as hydrogen-bonded dimers about crystallographic inversion centres.

Comment

4-Oxyalkyl-substituted benzoic acids are well known and their synthesis from the corresponding 4-hydroxybenzoic acids is facile. Structurally characterized examples include 4-*n*-heptyloxybenzoic acid, (2), 4-*n*-nonyloxybenzoic acid, (3), and 4-*n*-decyloxybenzoic acid, (4) (Bryan, Hartley, Miller & Shen, 1980). These compounds crystallize in the triclinic space group *P* $\bar{1}$, with very similar lattice parameters except for the *c* axis, the length of which varies with the length of the *n*-alkyl chain.



There are fewer structurally characterized examples of the corresponding acids with purely hydrocarbon chains (a reflection of the greater difficulty associated with their synthesis); 4-methylbenzoic acid (Takwale & Pant, 1971) and 4-*tert*-butylbenzoic acid (van Koningsveld, 1982) have been reported. In 4-*n*-heptylbenzoic acid, (1) (Fig. 1), the *n*-alkyl chain is fully extended, its conformation being all-*trans*. The plane of the chain is approximately orthogonal to that of the aromatic

ring. Overall, the molecule is bent with an angle of 143.36(5)° subtended at C7 between the axis of the alkyl chain and that passing through atoms C, C1*p* and C4*p* of the benzoic acid fragment (Fig. 1*b*). Within estimated error, the carboxylic acid group is coplanar with the aromatic ring.

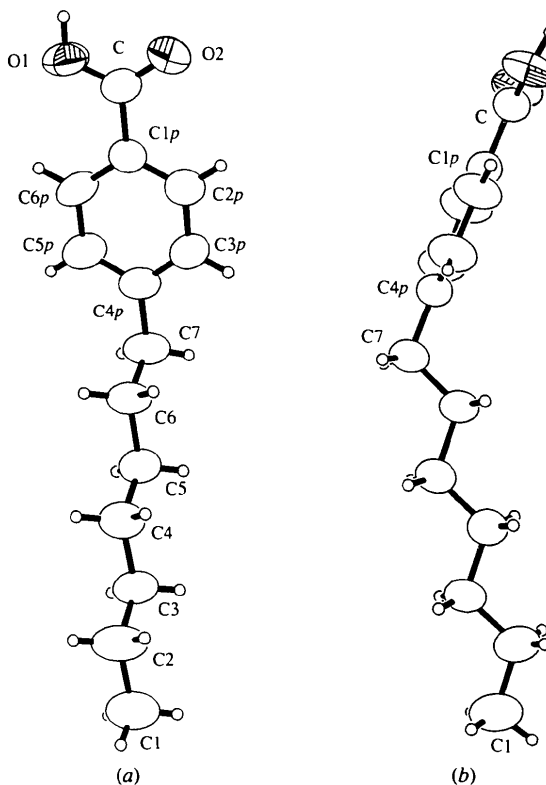


Fig. 1. Views of (a) a molecule of (1) and (b) the bending of the molecule at C7, with the atom-numbering scheme, displacement ellipsoids enclosing 50% electron probability surfaces and H atoms represented by spheres of arbitrary radii.

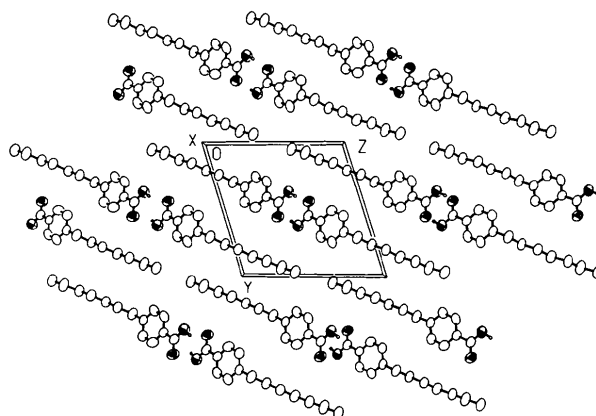


Fig. 2. A projection of the structure along [100] showing the hydrogen-bonded dimers. Molecules form stacks along the view direction with a separation of 4.848(3) Å. H atoms bound to C atoms have been omitted for clarity.

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The principal intermolecular interaction (Fig. 2) is the ubiquitous pairwise hydrogen bonding. This occurs across the inversion centre at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and is characterized by $\text{H1}\cdots\text{O2}'$ 1.72 (5) Å, $\text{C—O2}\cdots\text{H1}'$ 116 (2) and $\text{O1—H1}\cdots\text{O2}'$ 169 (5)°. The $\text{O1}\cdots\text{O2}'$ separation is 2.621 (5) Å. Molecules form stacks along the view direction of Fig. 2, with a separation of 4.848 (3) Å.

Experimental

4-*n*-Heptylbenzoyl chloride (Lancaster Synthesis) was hydrolysed with 10% aqueous NaOH in tetrahydrofuran solution and the product recrystallized from hot ethanol. Crystals were grown from a mixture of dichloromethane and *n*-heptane by concentration of the solution.

Crystal data

$\text{C}_{14}\text{H}_{20}\text{O}_2$
 $M_r = 220.30$
 Triclinic
 $P\bar{1}$
 $a = 4.848$ (3) Å
 $b = 11.790$ (7) Å
 $c = 12.159$ (5) Å
 $\alpha = 72.06$ (2)°
 $\beta = 84.77$ (3)°
 $\gamma = 84.19$ (4)°
 $V = 656.5$ (6) Å³
 $Z = 2$
 $D_x = 1.114$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 23 reflections
 $\theta = 6.5$ – 13 °
 $\mu = 0.073$ mm⁻¹
 $T = 295$ (2) K
 Plate
 $0.70 \times 0.27 \times 0.03$ mm
 Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
 ω - 2θ scans [width (1.2 + 0.35tan θ)° in ω]
 Absorption correction: none
 4708 measured reflections
 2300 independent reflections
 707 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.1099$
 $\theta_{\text{max}} = 25.06$ °
 $h = -5 \rightarrow 5$
 $k = -12 \rightarrow 13$
 $l = 0 \rightarrow 14$
 3 standard reflections
 frequency: 120 min
 intensity decay: 6%

Refinement

Refinement on F^2
 $R(F) = 0.0672$
 $wR(F^2) = 0.1610$
 $S = 0.961$
 2289 reflections
 146 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.048P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -0.001$
 $\Delta\rho_{\text{max}} = 0.12$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.12$ e Å⁻³

Extinction correction: *SHELXL93* (Sheldrick, 1993)
 Extinction coefficient: 0.019 (5)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C1	-0.3651 (11)	0.0470 (4)	-0.3830 (4)	0.106 (2)
C2	-0.2145 (11)	0.0758 (5)	-0.2939 (4)	0.102 (2)
C3	-0.3965 (9)	0.1243 (4)	-0.2100 (4)	0.0760 (15)
C4	-0.2385 (10)	0.1525 (4)	-0.1217 (4)	0.0790 (15)
C5	-0.4165 (9)	0.2067 (4)	-0.0385 (3)	0.0701 (14)
C6	-0.2541 (9)	0.2399 (4)	0.0462 (4)	0.0719 (14)
C7	-0.4233 (10)	0.2950 (4)	0.1280 (4)	0.080 (2)
C1 _p	0.0808 (9)	0.4109 (4)	0.3398 (4)	0.0588 (13)
C2 _p	-0.0128 (11)	0.4886 (4)	0.2395 (5)	0.093 (2)
C3 _p	-0.1749 (10)	0.4495 (5)	0.1721 (4)	0.086 (2)
C4 _p	-0.2522 (9)	0.3342 (5)	0.2040 (4)	0.0644 (14)
C5 _p	-0.1587 (10)	0.2590 (4)	0.3057 (4)	0.081 (2)
C6 _p	0.0049 (9)	0.2958 (5)	0.3731 (4)	0.078 (2)
C	0.2593 (10)	0.4521 (5)	0.4095 (4)	0.0668 (14)
O1	0.3367 (7)	0.3757 (3)	0.5023 (3)	0.0918 (12)
O2	0.3284 (7)	0.5571 (3)	0.3762 (3)	0.0944 (13)

Table 2. Selected geometric parameters (Å, °)

C1—C2	1.497 (5)	C1 _p —C6 _p	1.370 (5)
C2—C3	1.497 (6)	C1 _p —C	1.475 (5)
C3—C4	1.507 (5)	C2 _p —C3 _p	1.388 (5)
C4—C5	1.517 (5)	C3 _p —C4 _p	1.374 (5)
C5—C6	1.514 (5)	C4 _p —C5 _p	1.366 (5)
C6—C7	1.492 (5)	C5 _p —C6 _p	1.377 (5)
C7—C4 _p	1.496 (5)	C—O2	1.248 (5)
C1 _p —C2 _p	1.364 (5)	C—O1	1.268 (5)
C3—C2—C1	114.9 (4)	C4 _p —C3 _p —C2 _p	122.3 (5)
C2—C3—C4	113.6 (4)	C5 _p —C4 _p —C3 _p	116.5 (4)
C3—C4—C5	114.8 (4)	C5 _p —C4 _p —C7	122.9 (5)
C6—C5—C4	114.3 (4)	C3 _p —C4 _p —C7	120.6 (5)
C7—C6—C5	115.5 (4)	C4 _p —C5 _p —C6 _p	122.1 (4)
C6—C7—C4 _p	113.4 (4)	C1 _p —C6 _p —C5 _p	120.7 (4)
C2 _p —C1 _p —C6 _p	118.6 (4)	O2—C—O1	123.2 (4)
C2 _p —C1 _p —C	119.7 (5)	O2—C—C1 _p	120.3 (5)
C6 _p —C1 _p —C	121.7 (5)	O1—C—C1 _p	116.5 (5)
C1 _p —C2 _p —C3 _p	119.9 (5)		
C1—C2—C3—C4	-179.9 (4)	C6—C7—C4 _p —C3 _p	93.1 (5)
C2—C3—C4—C5	177.6 (4)	C2 _p —C1 _p —C—O2	-1.1 (7)
C3—C4—C5—C6	-177.3 (4)	C6 _p —C1 _p —C—O2	178.9 (5)
C4—C5—C6—C7	179.2 (4)	C2 _p —C1 _p —C—O1	179.3 (5)
C5—C6—C7—C4 _p	-175.9 (4)	C6 _p —C1 _p —C—O1	-0.6 (6)
C6—C7—C4 _p —C5 _p	-85.2 (6)		

H atoms were placed in calculated positions and allowed to ride on their respective C atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. In contrast, the positional parameters were refined freely for atom H1.

Data collection: *DIF4* (Stoe & Cie, 1990a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL93*.

We thank EPSRC for support and acknowledge use of the Cambridge Structural Database implemented at Daresbury Laboratory.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Redetermination of the Structures of 1,4,7-Trioxa-10,13-dithiacyclopentadecane and 1,4,7,10-Tetraoxa-13,16-dithiacyclooctadecane

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Abstract

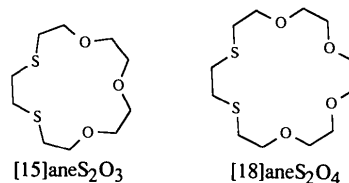
Both 1,4,7-trioxa-10,13-dithiacyclopentadecane, C₁₀H₂₀O₃S₂, and 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane, C₁₂H₂₄O₄S₂, show *exo*-oriented S and *endo*-oriented O atoms. The torsion angle of the SCH₂CH₂S moiety is *anti* [−165.93 (8)°] in the former and *gauche* [60.0 (2)°] in the latter. The latter exhibits C₂ symmetry through the midpoints of the C3—C3' and C11—C11' bonds.

Comment

We have been investigating the coordination chemistry of mixed O/S donor ionophores such as 1,4,7-trioxa-10,13-dithiacyclopentadecane (C₁₀H₂₀O₃S₂, [15]aneS₂O₃) and 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane (C₁₂H₂₄O₄S₂, [18]aneS₂O₄). Both ionophores have been found to adopt *endo* as well as *exo* coordination modes with a range of transition metal ions (Bell, 1987; Reid, 1989; Blake, Gould, Reid & Schröder, 1990; Blake, Reid & Schröder, 1990; Blake, Collison, Gould, Reid & Schröder, 1993; Blake, Gould, Radek & Schröder, 1994; Radek, 1995).

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We recently reported the single-crystal X-ray structure of 1,4,7,10,13-pentaoxa-16,19-dithiacyclohenicosane ([21]aneS₂O₅) sesquihydrate (Blake, Gould, Harris, Parsons, Radek & Schröder, 1995), which shows extended inter- and intramolecular hydrogen bonding with molecules of water of crystallization. As part of this study, we have redetermined the structures of the title compounds in order to improve on earlier structure determinations (Dalley, Larson, Smith, Matheson, Izatt & Christensen, 1981) and to establish whether hydration and similar extended hydrogen bonding are present in these structures.



The single-crystal X-ray structures of [15]aneS₂O₃ (Fig. 1) and [18]aneS₂O₄ (Fig. 2) do not exhibit any new features compared with the earlier structure determinations. The differences in bond lengths, angles and torsion angles are marginal but the estimated standard deviations were improved by a factor of up to four. A discussion of the conformation of these compounds has been given (Dalley, Larson, Smith, Matheson, Izatt & Christensen, 1975, 1981; Wolf, Hartman, Storey, Foxman & Cooper, 1987). It should be emphasized, however, that Wolf, Hartman, Storey, Foxman & Cooper (1987) consider an S—C—C—S *gauche* torsion angle to be destabilizing (repulsive *gauche* effect) whereas an O—C—C—O *gauche* torsion angle is considered to be stabilizing (attractive *gauche* effect). [15]aneS₂O₃ conforms to these conditions, while

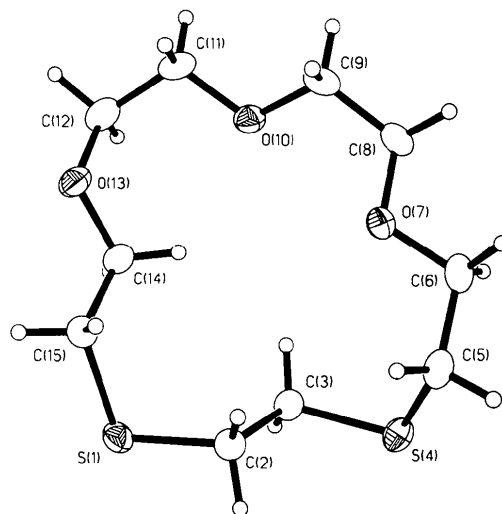


Fig. 1. The structure of the [15]aneS₂O₃ ionophore. Displacement ellipsoids enclose 50% probability surfaces.