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Acta Cryst. (1996). **C52**, 85–87

Attractive Edge–Face Arene–Arene Interactions in Combination with Close Packing of Alkoxy Chains for 1,4-Didecyloxybenzene

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(Received 20 June 1995; accepted 1 August 1995)

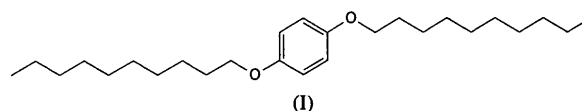
Abstract

The crystal structure of 1,4-didecyloxybenzene, C₂₆H₄₆O₂, displays a packing motif which is determined primarily by attractive edge–face arene–arene interactions and is cooperative with the close packing of the alkoxy chains. The oblique topology of the benzene moieties is essentially similar to that found for the homologous 1,4-dimethoxy and 1,4-diethoxy derivatives.

Comment

For many applications of simple π -conjugated compounds in material science, besides appropriate molecular properties, intermolecular π -overlap is an additional prerequisite. It is well established that numerous simple planar π -systems tend to aggregate edge–face in the solid state (Hunter, 1994, and references therein). Nevertheless, the intermolecular organization required for favourable π -overlap between constituents, *i.e.* a face–face orientation, may be induced *via* selective substitu-

tion with either long alkyl or alkoxy chains. Recently, we have shown by comparing solid-state packing motifs of 1,2,4,5-tetramethoxybenzene (herringbone-like; von Deuten & Klar, 1979) and 1,2,4,5-tetradecyloxybenzene (board-like; Keegstra *et al.*, 1995) that the introduction of the decyloxy chains markedly affects intermolecular interactions and hence intermolecular organization. As expected (Jorgensen & Severance, 1990, and references therein), no edge–face interactions are discernible in the case of 1,2,4,5-tetramethoxybenzene.



To gain insight to what extent this observation is affected by the number, length and substitution pattern of alkoxy chains, we decided to determine the single-crystal X-ray structure of 1,4-didecyloxybenzene. Single-crystal X-ray structures have been reported for the homologous 1,4-dimethoxybenzene (Goodwin, Przybylska & Robertson, 1950) and 1,4-diethoxybenzene (Haisa & Kashino, 1977). Edge–face interactions play an important role in determining their solid-state packing motif. As can be seen from Fig. 2, 1,4-didecyloxybenzene also possesses a packing motif which is primarily determined by attractive edge–face arene–arene interactions. The acute angle between the least-squares planes through the symmetry-related phenyl rings is 69.1 (2)°. The distance between the cen-

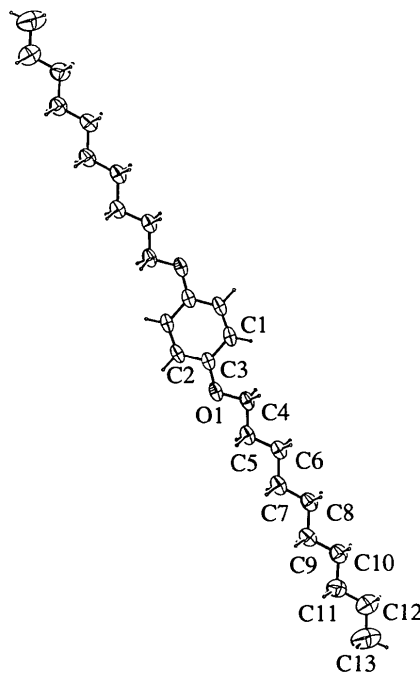


Fig. 1. Displacement ellipsoid plot (30% probability level) of 1,4-didecyloxybenzene.

tres of gravity of these rings is 4.781 (2) Å. The shortest non-bonded intermolecular distances between the rings are H2...C3 [$x, -\frac{1}{2} - y, -\frac{1}{2} + z$] = 2.834 (5) Å and H1...C1 [$x, \frac{1}{2} - y, \frac{1}{2} + z$] = 2.991 (5) Å. The first contact is 0.07 Å shorter than the sum of the van der Waals radii of carbon and hydrogen, whereas the second is 0.09 Å longer. The oblique topology of the benzene moieties is essentially similar to that found for the 1,4-dimethoxy and 1,4-diethoxy derivatives. The alkoxy chains display close packing in an orthorhombic subcell (Kitaigorodsky, 1973), as shown in Fig. 3.

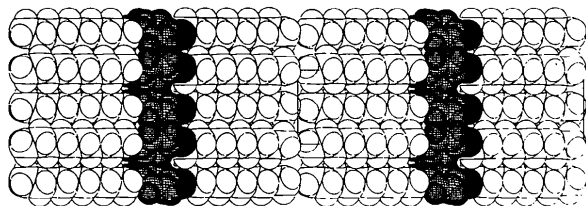


Fig. 2. Packing of 1,4-didecyloxybenzene projected down *c*, illustrating the edge-face interactions of the phenyl moiety and arrangement of the alkyl chains. The phenyl atoms are indicated with a net-like hatching, O atoms are black, alkoxy chains are white.

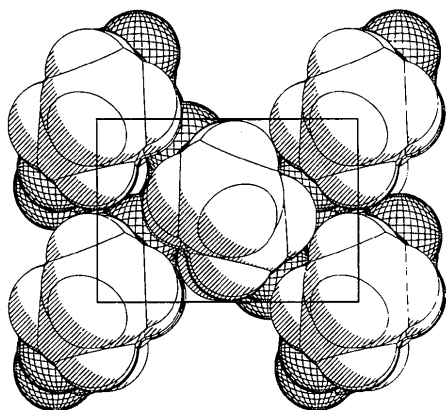


Fig. 3. Packing of 1,4-didecyloxybenzene projected down *a*, illustrating the close packing of the alkyl chains in an orthorhombic subcell.

Experimental

1,4-Didecyloxybenzene was synthesized from 1,4-dihydroxybenzene (0.10 mol) and 1-bromo-*n*-decane (0.201 mol) using potassium carbonate (0.25 mol) as base and dimethylformamide (250 ml) as solvent (Keegstra *et al.*, 1995). Yield: 36.3 g (0.093 mol, 93%) of a white crystalline solid. Satisfactory analytical data (¹H and ¹³C NMR, IR) were obtained. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane solution.

Crystal data

C₂₆H₄₆O₂
M_r = 390.65

Cu Kα radiation
λ = 1.54184 Å

Monoclinic
P2₁/c
a = 34.138 (13) Å
b = 7.3857 (11) Å
c = 6.072 (7) Å
β = 123.04 (3)°
V = 1283.4 (16) Å³
Z = 2
D_x = 1.011 Mg m⁻³

Data collection

Enraf–Nonius CAD-4F
diffractometer
ω/2θ scans
Absorption correction:
none
2430 measured reflections
2189 independent reflections
2189 observed reflections
[I ≥ -3σ(I)]

Refinement

Refinement on F²
R = 0.0681
wR = 0.1360
S = 1.823
2189 reflections
128 parameters
H-atom parameters not
refined
w = 1/[σ²(F_o²) + (0.0200P)²]
where P = [max(F_o², 0)
+ 2F_c²]/3

Cell parameters from 25
reflections
θ = 14.98–26.74°
μ = 0.46 mm⁻¹
T = 295 K
Plate
0.8 × 0.8 × 0.1 mm
Colourless

R_{int} = 0.1282
θ_{max} = 65.00°
h = -35 → 42
k = 0 → 9
l = -7 → 0
3 standard reflections
frequency: 60 min
intensity decay: 4%

(Δ/σ)_{max} = -0.002
Δρ_{max} = 0.13 e Å⁻³
Δρ_{min} = -0.14 e Å⁻³
Extinction correction: none
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)

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

	x	y	z	U _{eq}
O1	0.40881 (8)	-0.0283 (2)	0.8625 (3)	0.0808 (9)
C1	0.48829 (11)	0.0876 (3)	1.1576 (5)	0.0717 (14)
C2	0.46697 (11)	-0.0948 (3)	0.7845 (5)	0.0720 (14)
C3	0.45407 (12)	-0.0089 (4)	0.9353 (5)	0.0664 (12)
C4	0.39483 (10)	0.0393 (3)	1.0271 (5)	0.0789 (12)
C5	0.34712 (11)	-0.0324 (4)	0.9284 (5)	0.0855 (14)
C6	0.32440 (10)	0.0376 (3)	1.0644 (5)	0.0814 (12)
C7	0.27547 (11)	-0.0343 (4)	0.9513 (5)	0.0864 (14)
C8	0.25017 (11)	0.0370 (4)	1.0707 (6)	0.0896 (14)
C9	0.20096 (11)	-0.0353 (4)	0.9503 (6)	0.0948 (14)
C10	0.17468 (12)	0.0382 (4)	1.0635 (6)	0.1054 (16)
C11	0.12541 (12)	-0.0317 (5)	0.9376 (7)	0.1184 (17)
C12	0.0991 (2)	0.0463 (6)	1.0464 (8)	0.161 (3)
C13	0.0504 (2)	-0.0168 (6)	0.9192 (11)	0.240 (4)

Table 2. Selected geometric parameters (Å, °)

O1—C3	1.363 (5)	C1—C2'	1.369 (6)
O1—C4	1.413 (4)	C2—C3	1.369 (5)
C1—C3	1.405 (4)		
C3—O1—C4	119.6 (2)	O1—C3—C2	117.1 (3)
C2'—C1—C3	119.5 (3)	C1—C3—C2	118.4 (4)
C1'—C2—C3	122.1 (3)	O1—C4—C5	107.8 (2)
O1—C3—C1	124.5 (3)		

Symmetry code: (i) 1 - x, -y, 2 - z.

The unit-cell parameters were checked for the presence of higher lattice symmetry (Spek, 1988). Data were collected during 31 h of X-ray exposure time, with scan angle $\Delta\omega = (1.24 + 0.14 \tan \theta)^\circ$, horizontal aperture 3.83 mm, vertical aperture 6.00 mm. The space group was derived from observed systematic absences. R is calculated for 1115 reflections with $F > 4\sigma(F)$; wR is based on F^2 . H atoms were introduced at calculated positions, riding on their carrier atoms. The methyl group was refined as a rigid group, allowing for rotation around the C—C bond. H atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of the carrier atom by a factor of 1.5 for the methyl H atoms and 1.2 for all other H atoms.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *SET4* (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLUTON* (Spek, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1990).

This work was supported in part (ALS) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO), and by the Ministry of Economic Affairs of the Netherlands (IOP, EMDK).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1205). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 87–89

Methyl 3-(4-Methoxyphenylmethylene)dithiocarbazate

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(Received 9 May 1995; accepted 19 July 1995)

Abstract

The molecular conformation of the title compound, C₁₀H₁₂N₂OS₂, is almost planar. The structure is governed by N—H···S hydrogen bonds, leading to the formation of centrosymmetric dimers.

Comment

In recent years, many metal complexes of sulfur–nitrogen chelating agents have been studied (Ali & Bose, 1984; Ali, Hossain, Majumder & Uddin, 1987; Simon, 1994). Aside from showing interesting physicochemical properties, some of these complexes have been found to display carcinostatic activity (Sunl, 1985). This work is a continuation of our studies on metal complexes with ligands containing S and N as donor atoms (Fun, Sivakumar, Yip, Tian, Duan, Lu & You, 1995), and we now report the synthesis and crystal structure of a new Schiff-base compound derived from 4-methoxybenzaldehyde and methyl dithiocarbazate, *i.e.* methyl 3-(4-methoxyphenylmethylene)dithiocarbazate, (I).

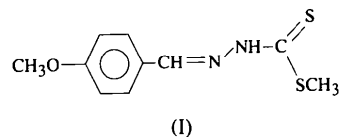


Fig. 1 shows an *ORTEP* plot (Johnson, 1965) of (I) with the atom-numbering scheme used. The molecule adopts an almost planar conformation. The largest torsion angle involving non-H atoms is $6.4(2)^\circ$ for C1—N1—N2—C2. Bond lengths and angles are normal except that the N1—C1 distance of 1.329(2) Å is shorter than the value typical of a single bond (*International Tables for Crystallography*, Vol. C, 1995). This is due to electron delocalization and was also observed in benzyl 3-(4-dimethylaminophenylmethylene)dithiocarbazate (Fun *et al.*, 1995).