The unusual molecular organization of 2,3-bis(*n*-hexyloxy)-anthracene in the crystal. A hint to the origin of the gelifying properties of 2,3-bis(*n*-alkyloxy)anthracenes?

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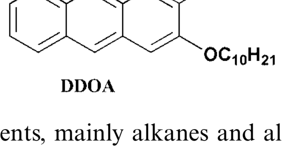
Received (in Cambridge, UK) 6th October 2000, Accepted 27th February 2001

Unlike most anthracene derivatives and other oblong shaped aromatics, 2,3-bis(*n*-hexyloxy)anthracene (DHOA) crystallizes in the space group $R(-3)$ with unit cell parameters $a = b = 14.639$, $c = 54.435$ Å. The molecular packing is composed of arrays of molecular triads. By computing the interaction potential of all the molecules with one another in space group $R(-3)$, the lowest energy structure is found to be a triad and the lowest energy layer a coplanar head-to-tail packing of these triads; most of the crystal energy is associated with the layer formation and the binding energy of the various structures is calculated to depend essentially on the non-bonded van der Waals interactions. They might prefigure the arrangement of the anthracene nuclei in the gel network nodes formed by 2,3-di-*n*-alkoxyanthracenes whose alkyl chains possess six or more carbon atoms.

Introduction

In recent years, there has been a considerable interest in the physical gels of organic liquids formed from *gelling agents* of *small molar mass* ($M_w \leq 1000$). A large number of new systems have been discovered by chance and their properties have been described.[1,2] This field was considered especially attractive because of the actual and potential applications of gels.[3–5] Moreover, the structures were expected to be simpler than those made from natural macromolecules or synthetic polymers,[4–7] and their structural principles thus to be more easily understood.

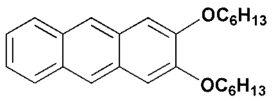
For the sake of simplicity, these systems can be divided in two main categories according to the driving force of network formation: *H-bonded* and *non-H-bonded* systems. In the second category, we emphasize the discovery by several of us[8] of the gelling properties of 2,3-bis(*n*-decyloxy)anthracene (DDOA) with diverse solvents, mainly alkanes and alcohols. Gelling of DDOA was found to be very efficient (at ambient temperature, a gel can be formed with methanol at concentration ≈7×10^{-4} M) and the gels are stable for months in stoppered vials. The gels were characterized by rheology in octanol as solid-like gels; moreover, neutron scattering (SANS) measurements and a WAXS diffraction experiment suggest that the structure of the crystalline junction zones is hexagonal.[9]



DDOA

A systematic investigation of the gelling ability of di-*n*-alkoxylanthracenes (in alkanes and alcohols) *at ambient temperature* as a function of the chain length showed that the number of carbons of each alkyl chain must be higher than or equal to 7.

In order to get a better insight into the gel structure (no clear picture of the molecular organization of the gel networks has been given so far, as discussed by Weiss *et al.*[10]), we attempted to grow single crystals. Unfortunately, the gel-forming molecules failed to produce crystalline materials under our conditions. However, we obtained single crystals suitable for X-ray structure determination with 2,3-bis(*n*-hexyloxy)anthracene (DHOA), which can also gelify organic fluids but at lower temperatures.



DHOA

To our surprise, DHOA proved to crystallize in space group $R(-3)$, an unexpected result for anthracene derivatives, which usually adopt $P2_1/c$ or other common monoclinic or orthorhombic space groups. No crystal structures are known of 2,3-substituted anthracenes, nor with two hexyloxy chains attached to any substrate. We here report the detailed crystal and molecular structure of DHOA and the results of semi-empirical calculations.

Results and discussion

As it was previously established that 2,3-dihydroxy-9,10-anthraquinone was the most suitable synthetic intermediate for preparation of 2,3-dialkoxyanthracene derivatives,[11] DHOA was then synthesized by a three-step procedure involving two reduction–dehydration steps ($NaBH_4$ in propan-2-ol, then HCl) from 2,3-bis(*n*-hexyloxy)-9,10-anthraquinone, readily obtained by alkylation of 2,3-dihydroxy-9,10-anthraquinone using 1-bromohexane and potassium carbonate in DMF.[12]

DOI: 10.1039/b008084p

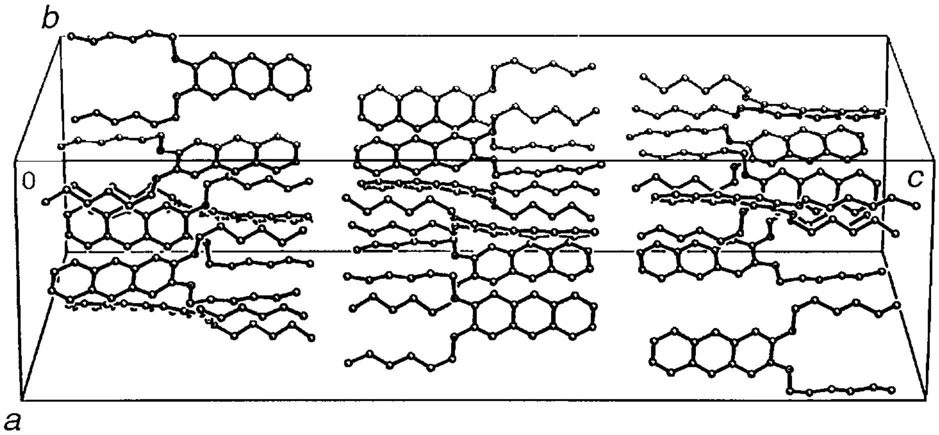


Fig. 1 Molecular packing of the 18 DHOA molecules in the unit cell.

Table 1 Selection of bond lengths (Å) and angles (°) of a single independent molecule of DHOA[a]

Bond	Bond length	Angle	
C(1)–C(2)	1.3523(23)	C(2)–C(1)–C(9A)	120.73(16)
C(1)–C(9A)	1.4340(23)	C(1)–C(2)–O(1)	127.14(16)
C(2)–O(1)	1.3624(19)	C(1)–C(2)–C(3)	120.04(17)
C(2)–C(3)	1.4518(22)	O(1)–C(2)–C(3)	112.81(15)
C(3)–C(4)	1.3528(23)	C(9A)–C(9)–C(8A)	121.93(17)
C(4)–C(4A)	1.4396(23)	C(9)–C(9A)–C(1)	121.94(17)
C(9)–C(9A)	1.3937(23)	C(9)–C(9A)–C(4A)	118.99(17)
O(1)–C(11)	1.4343(20)	O(1)–C(11)–C(12)	107.29(14)
O(2)–C(17)	1.4398(19)	C(13)–C(12)–C(11)	115.26(16)
C(11)–C(12)	1.5134(24)	C(12)–C(13)–C(14)	113.02(17)
C(12)–C(13)	1.5084(24)	C(15)–C(14)–C(13)	115.44(19)
C(13)–C(14)	1.5131(24)	C(16)–C(15)–C(14)	114.10(20)
C(14)–C(15)	1.5098(26)		
C(15)–C(16)	1.5030(29)		

[a] See Fig. 2 for numbering.

Table 2 Shortest intermolecular contacts; data are in Å, with esd's 0.002–0.003 Å. Symmetry operators: #1 $x-y$, $x-1$, $-z+1$; #2 $-y+1$, $x-y$, z; #3 $-x+1$, $-y$, $-z+1$; #4 $-x+y+1$, $-x+1$, z

C3–C17#1	3.391	C1–C12#3	3.687	C4A–C18#1	3.739
C3–C11#2	3.439	C2–C17#1	3.721	C9–C9#2	3.714
C4–C17#1	3.446	C2–C11#2	3.586	C9–C9#4	3.714
		C4A-C17#1	3.693	O2–C11#2	3.609

Structure determination[13]

Single crystals suitable for X-ray analysis were grown by slow evaporation of a heptane–dichloromethane solution.

Crystal data. Space group $R(-3)$, $a = b = 14.639(2)$, $c = 54.435(7)$ Å (hexagonal axes), $V = 10103$ Å^3, $Z = 18$, $D_x = 1.120$ Mg m^{-3}. Data from a hexagonal plate *ca.* 0.5 × 0.5 × 0.2 mm were measured at −100 °C on a Siemens P4 diffractometer using monochromated Mo-Kα radiation (ω scans, $2\theta_{max}$ 50°). The structure was refined on F^2 using the program[14] SHELXL-93. Hydrogen atoms were included using rigid methyl groups or a riding model. The final $wR2$ was 0.095, with conventional $R1$ 0.041, for all 3968 data, 255 parameters and 248 restraints; $S = 0.83$, max. $\Delta\rho$ 0.15 e Å^{-3}.

X-Ray crystal structure

The unit cell of DHOA, containing 18 molecules, is represented in Fig. 1. The molecule of DHOA displays the shape of a fish with a wide open bifid tail as shown in Fig. 2. The anthracene nucleus is planar within experimental errors. As shown from a selection of data (Table 1), bond lengths and angles do not exhibit abnormal features. The shortest intermolecular distances are shown in Table 2.

Table 3 Energy computation of the DHOA structure in space group R(−3); data in kcal mol^{-1}

	vdW	Coulomb	Total
Triad energy	−14.6	−0.52	−15.12
Triad layer	−42.72	−1.37	−44.09
Crystal $R(-3)$	−48.89	−1.34	−50.23

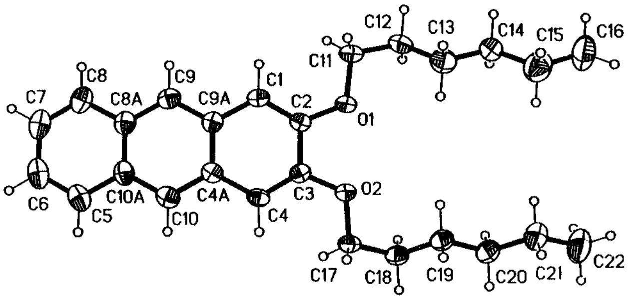


Fig. 2 The single independent molecule of DHOA in the crystal. Ellipsoids correspond to 50% probability. Hydrogen atom radii are arbitrary.

Molecular modelling

The molecular packing energy computation was conducted according to a method fully detailed in previous papers[15] using the MM2 force field Allinger program.[16] The analysis was performed by first packing the molecule in space group $R(-3)$ and then computing the interaction potential of all the molecules with one another; this computation makes no assumptions as to the *lowest energy structure*. The latter turns out to be a triad, as found experimentally. The *lowest energy layer* is a packing of these triads in a plane with inversion symmetry and repeat distance equal to the *a-b* unit cell repeats. The van der Waals (vdW), coulomb and total energies of molecules are collected in Table 3.

Comments

(a) The electrostatic energy is small compared to the vdW energy. Thus the binding energy of the various structures is determined by the non-bonded vdW interactions, as is generally found for most organic structures that do not have H-bonds. One would have expected an important contribution of the dipole moment ($\mu \simeq 1.9$ D) of DHOA to the packing energy; this dipole–dipole interaction would have induced a pairwise mutual head-to-tail orientation of the molecules which is clearly not the case. However the dipole–dipole interaction seems to be reflected in the head-to-tail orientation between the triads.

(b) Most of the crystal energy is found in the layer formation; the layers pack together to form the crystal with only an additional 6 kcal of energy lowering (−44 to −50). This is quite small; 88% of the crystal energy is tied up in the formation of the layer. The crystals must be lamellar in character.

(c) The triad energy reported in Table 3 is the average energy per molecule in the triad on a mole basis; the energy of the triad would thus be 3 times this number. The triad is clearly well-packed.

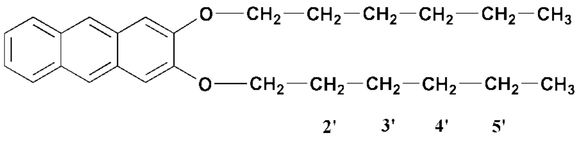
Conclusion

It is tempting to extrapolate these results by postulating that an increase of the hydrocarbon chain length should prevent a 3D crystalline packing and favour a 2D molecular arrangement, which might be the first step towards the formation of filaments and fibres. At this stage, the similarity of the UV spectra of DHOA (in KBr pellets) and DDOA (in the gel state) and of some IR vibrations (in both states),[17] suggests that the aromatic nuclei have on a short range similar structural arrangements in the DHOA crystals and in the DDOA gels' junction zones. Experiments are underway to test these hypotheses.

Experimental

2,3-Bis(*n*-hexyloxy)anthracene

According to the general reduction procedure previously described,[11] 2,3-bis(*n*-hexyloxy)-9,10-anthraquinone (1.06 g, 2.6 mmol) led to 0.61 g (62%) of DHOA after chromatography on silica gel, eluent: petroleum ether–dichloromethane 70/30 (v/v); mp 112 °C (pentane), colourless crystals (Found: C, 82.60; H 8.96. $C_{26}H_{34}O_2$ requires C, 82.54; H 8.99); δ_H (250 MHz; $CDCl_3$) 8.26 (2H, s, 9-H, 10-H), 8.00 (2H, m, 5-H, 8-H), 7.48 (2H, m, 6-H, 7-H), 7.24 (2H, s, 1-H, 4-H), 4.20 (4H, t, *J* 6.4, OCH_2), 2.01 (4H, m, $OCH_2C\mathit{H}_2$), 1.65 (4H, m, $OCH_2CH_2C\mathit{H}_2$), 1.50 (8H, m, $C\mathit{H}_2C\mathit{H}_2CH_3$), 1.04 (6H, t, *J* 6.7, CH_3); δ_C (62.5 MHz; $CDCl_3$) 150.1 (C2, C3), 103.8 (C8a, C10a), 128.8 (C4a, C9a), 127.7 (C5, C8), 124.5 (C6, C7), 123.8 (C9, C10), 105.9 (C1, C4), 68.7 (OCH_2), 31.8 (C4′), 29.1 (C2′), 25.9 (C3′), 22.8 (C5′), 14.2 (CH_3); ν_{max} 3050, 2916, 2850, 1630, 1570, 1490, 1470, 1400, 1390, 1290, 1225, 1195, 1170, 880 and 730 cm^{-1}; *m*/*z* 378.1 (M^+; 100%), 294 (17) and 210.1 (49).



Acknowledgements

We are grateful to Professor Fred Lewis for his suggestions and to Dr M. Cotrait and Professor P. Marsau for interesting discussions.

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