Crystal structure of *N*-n-dodecyl-bis(anthrylmethyl)amine, $C_{42}H_{47}N$

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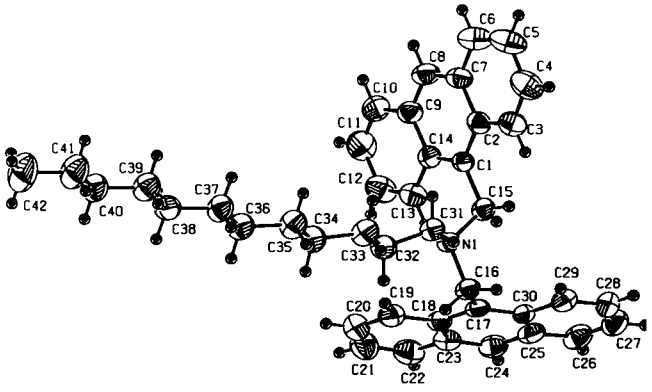

Abstract

$C_{42}H_{47}N$, triclinic, $P\bar{1}$ (No. 2), a = 10.011(4) Å, b = 10.265(2) Å, c = 17.139(8) Å, α = 72.32(2)°, β = 80.76(5)°, γ = 81.11(3)°, V = 1645.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.050, $wR_{ref}(F^2)$ = 0.180, T = 293 K.

Source of material

The title compound was obtained by refluxing for 5 hr in a two neck round bottom flask n-dodecylamine (1.00 g; 0.00539 mol) and 9-chloromethylanthracene (1.22 g; 0.00539 mol) in 150 ml dry dichloromethane. After that time, triethylamine (1 ml) was added and the crude mixture was chromatographed (TLC) in silica using pure chloroform as eluent. The less polar product (rf = 0.83 in silica/chloroform) was collected as a yellow powder and recrystalized by slow diffusion between dichloromethane and hexane, giving the title amine in 15% yield. Melting point: 390 K – 393 K.

Experimental details

The H-atoms of the organic moiety were placed at calculated positions and refined as riding using SHELXL-97 [1] defaults.

Discussion

The title compound was prepared within a project of developing highly ordered molecular films having specific electronic properties [2-5]. In particular, this compound was synthesised with the aim of studying the energy transfer processes between aromatic molecules included in the structure of new Langmuir-Blodgett films.

The molecules are arranged in layers, head to head, with the hydrocarbon chains side by side. The orientation of the anthracene groups is such that the two C1–C14 rings related by the inversion center are facing each other. The angle between the least-squares planes of the two anthracene groups is 67.67(7)° and the angles between these planes and the least-squares plane of the dodecyl chain are 69.87(9)° and 5.27(13)°, for rings C1–C14 and C17–C30 respectively. There is an in-plane bending of the substituted anthracenes, as shown by the somewhat larger valency angles C1–C2–C3 124.2(3)° [C17–C18–C19 123.1(3)°] and C1–C14–C13 122.8(3)° [C17–C30–C29 123.4(3)°] compared to the corresponding valency angles C8–C7–C6 120.6(3))° [C24–C23–C22 121.4(3)°] and C8–C9–C10 121.9(3)° [C24–C25–C26 122.1(3)°]. The deviations of the C atoms of the anthracene groups from the least squares plane of the corresponding 14-membered ring are smaller than in [5] but larger than those found in the unsubstituted anthracene molecule where the deviations do not exceed 0.010(2) Å [6]. The maximum deviation in ring C1–C14 is 0.029(3) Å (C5), in ring C17–C30 it is 0.067(3) Å (C27).

The conformation of the zigzag dodecyl chain in the title compound is completely *trans*, the largest deviation being 15.1(3)° for the C31–C32–C33–C34 torsion angle. The values of the bond lengths and angles of the chain agree well with those observed in other long-chain structures [6,7]. The N—C distances are 1.465(3) Å, 1.468(3) Å and 1.474(3) Å, the C–N1–C angles range from 110.4(2)° to 112.5(2)°. The structure is stabilized by six C—H···π intermolecular interactions, which does not saturate the H-bonding capability of the aromatic π electron clouds as found in other similar anthracene compounds [5]. Two of the bonds adopt a classical T-shape arrangement (α greater than 150°, θ angle greater than 80°), with short hydrogen to ring centroid distances C27—H27···Cg(1)^{i} 2.586 Å and C8—H8···Cg(6)^{ii} 2.987 Å [Cg(1) and Cg(2) are the ring centroids of the 6-membered rings C1–C14 and C2–C7, respectively; symmetry codes: (*i*) x, 1+y, z; (*ii*) –x, 1–y,1–z]. Four other C—H···π intermolecular interactions are present in the structure, one of type III and three of type V according to the definitions in [8]. Direct π···π interactions may also be relevant in determining the crystal packing, the shortest distance between two rings is 3.899(3) Å between Cg(1) and Cg(3)^{iii} [Cg(3) is the ring centroid of the 6-membered ring C9–C14; symmetry code: (*iii*) 1–x,1–y,1–z].

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Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.1 × 0.25 × 0.45 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.65 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD-4, ω/θ
$2\theta_{max}$:	50.14°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6182, 5819
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2700
$N(param)_{refined}$:	389
Programs:	SHELXL-97 [1], SHELXS-97 [9], PLATON [10], ORTEPII [11]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	2*i*	–0.2554	0.6740	0.3156	0.069
H(4)	2*i*	–0.4616	0.7792	0.3529	0.090
H(5)	2*i*	–0.4919	0.8851	0.4577	0.097
H(6)	2*i*	–0.3132	0.8864	0.5234	0.084
H(8)	2*i*	–0.0766	0.8197	0.5453	0.068
H(10)	2*i*	0.1634	0.7561	0.5695	0.075
H(11)	2*i*	0.3706	0.6451	0.5411	0.088
H(12)	2*i*	0.4068	0.5279	0.4420	0.082
H(13)	2*i*	0.2380	0.5252	0.3696	0.063
H(15A)	2*i*	0.0404	0.4692	0.3403	0.054
H(15B)	2*i*	–0.0802	0.5633	0.2960	0.054
H(16A)	2*i*	0.1992	0.5797	0.1418	0.055
H(16B)	2*i*	0.0625	0.5137	0.1741	0.055
H(19)	2*i*	0.3759	0.6042	0.1989	0.069
H(20)	2*i*	0.5924	0.5978	0.2229	0.084
H(21)	2*i*	0.7178	0.3915	0.2854	0.091
H(22)	2*i*	0.6238	0.1906	0.3195	0.082
H(24)	2*i*	0.4306	0.0674	0.3262	0.066
H(26)	2*i*	0.2343	–0.0602	0.3455	0.075
H(27)	2*i*	0.0127	–0.0630	0.3345	0.080
H(28)	2*i*	–0.1173	0.1396	0.2720	0.078
H(29)	2*i*	–0.0274	0.3424	0.2249	0.065
H(31A)	2*i*	–0.0106	0.8066	0.2320	0.056
H(31B)	2*i*	–0.0037	0.7511	0.1556	0.056
H(32A)	2*i*	0.2186	0.8070	0.1124	0.064
H(32B)	2*i*	0.2164	0.8576	0.1902	0.064
H(33A)	2*i*	0.0733	0.9904	0.0539	0.068
H(33B)	2*i*	0.0322	1.0299	0.1366	0.068
H(34A)	2*i*	0.2494	1.0977	0.1252	0.069
H(34B)	2*i*	0.2886	1.0603	0.0419	0.069
H(35A)	2*i*	0.0833	1.2717	0.0620	0.075
H(35B)	2*i*	0.1373	1.2390	–0.0218	0.075
H(36A)	2*i*	0.2999	1.3360	0.0636	0.072
H(36B)	2*i*	0.3453	1.3130	–0.0234	0.072
H(37A)	2*i*	0.1904	1.4957	–0.0817	0.074
H(37B)	2*i*	0.1348	1.5155	0.0052	0.074
H(38A)	2*i*	0.3975	1.5662	–0.0761	0.072
H(38B)	2*i*	0.3479	1.5793	0.0129	0.072
H(39A)	2*i*	0.2326	1.7495	–0.1286	0.078
H(39B)	2*i*	0.1875	1.7639	–0.0395	0.078
H(40A)	2*i*	0.3935	1.8354	–0.0378	0.078
H(40B)	2*i*	0.4484	1.8097	–0.1233	0.078
H(41A)	2*i*	0.2380	2.0149	–0.1009	0.104
H(41B)	2*i*	0.2930	1.9892	–0.1864	0.104
H(42A)	2*i*	0.4474	2.0831	–0.0954	0.161
H(42B)	2*i*	0.3848	2.1756	–0.1749	0.161
H(42C)	2*i*	0.5022	2.0577	–0.1811	0.161

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	2*i*	0.1028(2)	0.6245(2)	0.2439(1)	0.054(2)	0.033(1)	0.033(1)	–0.003(1)	0.001(1)	–0.010(1)
C(1)	2*i*	–0.0199(3)	0.6407(2)	0.3802(2)	0.049(2)	0.031(1)	0.034(2)	–0.007(1)	0.005(1)	–0.006(1)
C(2)	2*i*	–0.1502(3)	0.7073(3)	0.3993(2)	0.047(2)	0.040(2)	0.041(2)	–0.006(1)	0.001(1)	–0.006(1)
C(3)	2*i*	–0.2649(3)	0.7142(3)	0.3584(2)	0.053(2)	0.062(2)	0.056(2)	0.000(2)	–0.005(2)	–0.017(2)
C(4)	2*i*	–0.3881(4)	0.7780(4)	0.3802(2)	0.056(2)	0.087(3)	0.070(2)	0.005(2)	–0.008(2)	–0.012(2)
C(5)	2*i*	–0.4067(4)	0.8424(4)	0.4432(2)	0.069(3)	0.090(3)	0.065(2)	0.025(2)	0.005(2)	–0.018(2)
C(6)	2*i*	–0.3007(4)	0.8420(4)	0.4824(2)	0.074(3)	0.074(2)	0.056(2)	0.017(2)	–0.002(2)	–0.023(2)
C(7)	2*i*	–0.1704(3)	0.7755(3)	0.4627(2)	0.057(2)	0.048(2)	0.041(2)	0.000(2)	0.004(2)	–0.012(1)
C(8)	2*i*	–0.0625(3)	0.7751(3)	0.5044(2)	0.073(2)	0.056(2)	0.041(2)	–0.006(2)	0.004(2)	–0.020(2)
C(9)	2*i*	0.0657(3)	0.7102(3)	0.4868(2)	0.063(2)	0.050(2)	0.038(2)	–0.010(2)	0.002(2)	–0.012(1)
C(10)	2*i*	0.1763(4)	0.7099(4)	0.5294(2)	0.070(3)	0.076(2)	0.050(2)	–0.013(2)	–0.009(2)	–0.026(2)
C(11)	2*i*	0.2994(4)	0.6441(4)	0.5125(2)	0.070(3)	0.099(3)	0.057(2)	–0.017(2)	–0.016(2)	–0.023(2)
C(12)	2*i*	0.3212(4)	0.5739(4)	0.4524(2)	0.055(2)	0.087(3)	0.058(2)	0.003(2)	–0.010(2)	–0.018(2)
C(13)	2*i*	0.2205(3)	0.5719(3)	0.4095(2)	0.055(2)	0.053(2)	0.046(2)	0.001(2)	–0.003(2)	–0.011(2)
C(14)	2*i*	0.0874(3)	0.6400(3)	0.4242(2)	0.053(2)	0.037(2)	0.035(2)	–0.006(1)	–0.002(1)	–0.005(1)
C(15)	2*i*	0.0056(3)	0.5639(3)	0.3152(2)	0.055(2)	0.037(2)	0.041(2)	–0.008(1)	–0.001(1)	–0.010(1)
C(16)	2*i*	0.1436(3)	0.5327(3)	0.1911(2)	0.061(2)	0.039(2)	0.036(2)	–0.006(1)	–0.002(1)	–0.012(1)
C(17)	2*i*	0.2223(3)	0.3976(3)	0.2324(2)	0.049(2)	0.040(2)	0.037(2)	–0.001(1)	–0.000(1)	–0.018(1)
C(18)	2*i*	0.3579(3)	0.3976(3)	0.2450(2)	0.053(2)	0.042(2)	0.040(2)	–0.004(1)	0.004(1)	–0.016(1)
C(19)	2*i*	0.4234(3)	0.5201(3)	0.2234(2)	0.061(2)	0.052(2)	0.059(2)	–0.005(2)	0.003(2)	–0.021(2)
C(20)	2*i*	0.5527(4)	0.5162(4)	0.2379(2)	0.057(2)	0.079(3)	0.081(3)	–0.016(2)	0.002(2)	–0.034(2)
C(21)	2*i*	0.6293(4)	0.3917(4)	0.2751(2)	0.053(2)	0.098(3)	0.084(3)	–0.013(2)	–0.006(2)	–0.036(2)
C(22)	2*i*	0.5728(4)	0.2730(4)	0.2958(2)	0.060(2)	0.078(3)	0.065(2)	0.006(2)	–0.007(2)	–0.025(2)
C(23)	2*i*	0.4370(3)	0.2713(3)	0.2822(2)	0.050(2)	0.053(2)	0.048(2)	0.003(2)	–0.002(1)	–0.020(2)
C(24)	2*i*	0.3783(3)	0.1498(3)	0.3041(2)	0.064(2)	0.045(2)	0.053(2)	0.009(2)	–0.006(2)	–0.016(2)
C(25)	2*i*	0.2450(3)	0.1463(3)	0.2945(2)	0.069(2)	0.038(2)	0.042(2)	0.001(2)	–0.001(2)	–0.016(1)
C(26)	2*i*	0.1826(4)	0.0218(3)	0.3220(2)	0.093(3)	0.039(2)	0.053(2)	–0.005(2)	–0.004(2)	–0.013(2)
C(27)	2*i*	0.0515(4)	0.0193(3)	0.3149(2)	0.094(3)	0.049(2)	0.060(2)	–0.022(2)	0.004(2)	–0.018(2)
C(28)	2*i*	–0.0269(4)	0.1419(3)	0.2776(2)	0.069(2)	0.064(2)	0.068(2)	–0.023(2)	0.004(2)	–0.029(2)
C(29)	2*i*	0.0269(3)	0.2631(3)	0.2497(2)	0.062(2)	0.047(2)	0.059(2)	–0.005(2)	–0.002(2)	–0.024(2)
C(30)	2*i*	0.1641(3)	0.2724(3)	0.2573(2)	0.048(2)	0.041(2)	0.039(2)	–0.008(1)	0.003(1)	–0.019(1)
C(31)	2*i*	0.0496(3)	0.7612(3)	0.1955(2)	0.057(2)	0.037(2)	0.041(2)	–0.001(1)	–0.005(1)	–0.008(1)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(32)	2*i*	0.1607(3)	0.8510(3)	0.1504(2)	0.062(2)	0.043(2)	0.049(2)	–0.006(2)	0.001(2)	–0.010(1)
C(33)	2*i*	0.1078(3)	0.9950(3)	0.1027(2)	0.076(2)	0.041(2)	0.046(2)	–0.005(2)	–0.011(2)	–0.003(1)
C(34)	2*i*	0.2138(3)	1.0950(3)	0.0764(2)	0.071(2)	0.044(2)	0.051(2)	–0.011(2)	–0.004(2)	–0.004(1)
C(35)	2*i*	0.1638(4)	1.2399(3)	0.0300(2)	0.084(2)	0.048(2)	0.051(2)	–0.014(2)	–0.010(2)	–0.002(2)
C(36)	2*i*	0.2679(3)	1.3410(3)	0.0122(2)	0.078(2)	0.045(2)	0.053(2)	–0.010(2)	–0.003(2)	–0.008(2)
C(37)	2*i*	0.2160(3)	1.4892(3)	–0.0283(2)	0.078(2)	0.045(2)	0.059(2)	–0.012(2)	–0.004(2)	–0.009(2)
C(38)	2*i*	0.3184(3)	1.5897(3)	–0.0401(2)	0.074(2)	0.047(2)	0.052(2)	–0.011(2)	0.005(2)	–0.010(2)
C(39)	2*i*	0.2648(4)	1.7396(3)	–0.0764(2)	0.082(2)	0.048(2)	0.062(2)	–0.010(2)	–0.009(2)	–0.011(2)
C(40)	2*i*	0.3676(4)	1.8391(3)	–0.0907(2)	0.080(2)	0.049(2)	0.063(2)	–0.016(2)	–0.003(2)	–0.012(2)
C(41)	2*i*	0.3188(4)	1.9854(3)	–0.1335(3)	0.113(3)	0.052(2)	0.091(3)	–0.020(2)	–0.015(2)	–0.009(2)
C(42)	2*i*	0.4227(5)	2.0845(4)	–0.1475(3)	0.145(4)	0.063(3)	0.109(3)	–0.039(3)	–0.016(3)	–0.004(2)

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