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2,3,10,11-Tetramethoxy-6,7,14,15-tetrahydro-6,14-methanocycloocta-[1,2-*b*;5,6-*b*′]diquinoline

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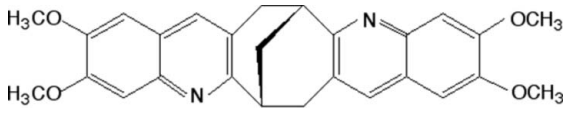
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.006 Å; R factor = 0.050; wR factor = 0.053; data-to-parameter ratio = 5.4.

The racemic title compound, $C_{27}H_{26}N_2O_4$, crystallizes with its central carbon bridge on a twofold axis. It forms parallel chains of molecules utilizing aryl offset face–face interactions with an interplanar distance of about 3.5 Å. These chains associate further by means of pairs of O—CH_2—H$\cdots\pi$ (with H–ring distances ranging from 2.69 to 2.95 Å) and O—CH_2—H$\cdots$N motifs. The methoxy groups in this structure are coplanar with the aromatic rings to which they are attached. This is recognized as being common behaviour amongst aromatic methoxy compounds.

Related literature

Condensation of two equivalents of a 2-aminobenzaldehyde derivative with one of bicyclo[3.3.1]nonane-2,6-dione provides a V-shaped diquinoline adduct by means of the Friedländer condensation (Cheng & Yan, 1982). Substituted molecules of this general structural type frequently act as lattice inclusion hosts (Bishop, 2006). For related literature, see: Allen (2002); Desiraju & Gavezzotti (1989); Marjo *et al.* (1997); Pendrak *et al.* (1995); Schaefer & Honig (1968).



Experimental

Crystal data

$C_{27}H_{26}N_2O_4$
M_r = 442.5
Monoclinic, $C2/c$
a = 14.137 (7) Å
b = 9.533 (6) Å
c = 16.551 (7) Å
β = 100.79 (3)°
V = 2191 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 294 K
0.12 mm (radius)

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
1999 measured reflections
1926 independent reflections
803 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
1 standard reflection
frequency: 30 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.053
S = 1.41
803 reflections
150 parameters
H-atom parameters not refined
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C14—H3C14$\cdots$N1^{i}	1.00	2.88	3.723 (5)	142
C14—H3C14$\cdots$N1^{ii}	1.00	2.96	3.348 (5)	104

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $x-\frac{1}{2}, y-\frac{1}{2}, z$.

Data collection: *CAD-4 Software* (Schagen *et al.*, 1989); cell refinement: *CAD-4 Software*; data reduction: Local program; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *RAELS* (Rae, 2000); molecular graphics: *ORTEPII* (Johnson, 1976) and *CrystalMaker* (CrystalMaker, 2005); software used to prepare material for publication: Local programs.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LN2008).

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supplementary materials

Acta Cryst. (2008). E**64**, o48 [**doi:10.1107/S1600536807061235**]

2,3,10,11-Tetramethoxy-6,7,14,15-tetrahydro-6,14-methanocycloocta[1,2-*b*;5,6-*b*']diquinoline

J. Ashmore, R. Bishop, D. C. Craig and M. L. Scudder

Comment

The asymmetric unit of the title compound, (1), contains half a molecule, with the central bridging carbon atom located on a twofold axis (Fig. 1).

Molecules of (1) form parallel chains along the *ac* diagonal (Fig. 2), associating by means of *exo,exo*-facial aryl offset face-face (OFF) interactions (Desiraju & Gavezzotti, 1989). The distance between the aromatic planes is about 3.5 Å. Complementary to the π···π interaction are a pair of associations between a methoxy group and a quinoline N atom (O—CH_2—H···N; d = 2.88 Å), and a pair between an aliphatic methylene and a methoxy group (C—H···O—CH_3, d = 2.84 Å). Adjacent chains interact in two ways: by means of a double centrosymmetric O—CH_2—H···π interaction (utilizing the 3-methoxy group, with shortest C···C contacts of 3.57 and 3.82 Å) and an O—CH_2—H···N interaction (utilizing the 10-methoxy group with C···N of 3.35 Å).

It is noteworthy that the methoxy groups in this structure are co-planar with the aromatic rings to which they are attached. The Cambridge Structural Database (Allen *et al.*, 2002) reveals that this situation is commonplace amongst related compounds. The steric effects resulting from this co-planarity would be sufficient cause for the absence of centrosymmetric dimers utilizing the edge-edge aryl C—H···N supramolecular synthon which are found in the parent the non-methoxy diquinoline adduct (Marjo *et al.*, 1997).

Experimental

2-Amino-4,5-dimethoxybenzaldehyde (Pendrak *et al.*, 1995) (1.20 g, 6.62 mmol) and bicyclo[3.3.1]nonane-2,6-dione (Schaefer & Honig, 1968) (0.38 g, 2.50 mol) were dissolved in hot ethanol (20 ml) and a solution of sodium hydroxide (0.49 g, 12.25 mmol) in ethanol (10 ml) was added. The mixture was refluxed for 5 h, allowed to cool, then kept at 273 K for 5 h. Filtration gave the product 1 (0.51 g, 46%) of m.p. 548–549 K. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 29.5 (CH_2), 36.6 (CH), 38.2 (CH_2), 56.2 (CH_3), 56.4 (CH_3), 104.6 (CH), 107.4 (CH), 123.3 (C), 126.8 (C), 134.7 (CH), 144.3 (C), 149.7 (C), 152.3 (C), 159.2 (C); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.49 (br s, 2H), 3.25 & 3.32 (d, 2H, J_{AB} 16.6 Hz), 3.42 & 3.49 (dd, 2H, J_{AB} 16.6, J_{BX} 5.3 Hz), 3.70 (d, 2H, J 2.6 Hz), 3.91 (s, 6H), 3.99 (s, 6H), 6.79 (s, 2H), 7.32 (s, 2H), 7.50 (s, 2H). X-ray quality crystals were obtained from ethyl acetate solution.

Refinement

All hydrogen atoms were placed geometrically with C—H = 1.0 Å and U_{iso}(H) = U_{eq}(C).

Figures

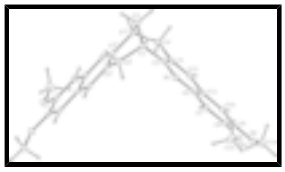


Fig. 1. Molecular structure of (1), with ellipsoids drawn at 30% probability level. Symmetry code: (i) $1 - x, y, 3/2 - z$.

Fig. 2. The chain of molecules of (1) with centrosymmetric OFF interactions between *exo*-surfaces of the aromatic wings. Adjacent molecules are of the opposite chirality.

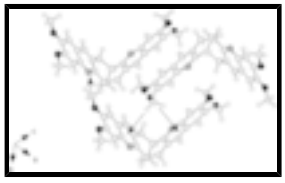


Fig. 3. The chain (top) interacts with adjacent chains in two ways: a double $CH_3\cdots\pi$ interaction (pair of arrows at the bottom of the figure) and a $CH_3\cdots N$ interaction (at the left of the figure).

2,3,10,11-Tetramethoxy-6,7,14,15-tetrahydro-6,14- methanocycloocta[1,2 – *b*;5,6-*b*′]diquinoline

Crystal data

$C_{27}H_{26}N_2O_4$	F_{000} = 936.0
M_r = 442.5	D_x = 1.34 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
a = 14.137 (7) Å	Cell parameters from 11 reflections
b = 9.533 (6) Å	θ = 10–11º
c = 16.551 (7) Å	μ = 0.09 mm^{-1}
β = 100.79 (3)º	*T* = 294 K
V = 2191 (2) Å^3	Irregular, colourless
Z = 4	0.12 mm (radius)

Data collection

Enraf–Nonius CAD-4 diffractometer	θ_{max} = 25º
ω–2θ scans	*h* = −16→16
Absorption correction: none	*k* = 0→11
1999 measured reflections	*l* = 0→19
1926 independent reflections	1 standard reflections
803 reflections with $I > 2\sigma(I)$	every 30 min
R_{int} = 0.062	intensity decay: none

Refinement

Refinement on *F*	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)]$ = 0.050	$w = 1/[\sigma^2(F) + 0.0004F^2]$
$wR(F^2)$ = 0.053	$(\Delta/\sigma)_{max}$ = 0.001

S = 1.41	$\Delta\rho_{max}$ = 0.56 e Å^{-3}
803 reflections	$\Delta\rho_{min}$ = −0.48 e Å^{-3}
150 parameters	Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.3447 (2)	−0.0160 (3)	0.3564 (2)	0.059 (1)	
O2	0.2109 (2)	−0.1040 (3)	0.4273 (2)	0.0559 (9)	
N1	0.4643 (2)	0.2977 (4)	0.5789 (2)	0.047 (1)	
C1	0.5320 (4)	0.4581 (5)	0.6853 (3)	0.055 (1)	
C2	0.4554 (3)	0.3525 (4)	0.6509 (3)	0.043 (1)	
C3	0.3824 (3)	0.3145 (5)	0.6937 (3)	0.045 (1)	
C4	0.3736 (3)	0.3841 (5)	0.7746 (3)	0.054 (1)	
C5	0.5000	0.5529 (7)	0.7500	0.062 (2)	
C6	0.3986 (3)	0.1982 (4)	0.5451 (3)	0.041 (1)	
C7	0.4076 (3)	0.1425 (5)	0.4682 (2)	0.042 (1)	
C8	0.3440 (3)	0.0430 (5)	0.4314 (3)	0.043 (1)	
C9	0.2697 (3)	−0.0039 (5)	0.4705 (3)	0.042 (1)	
C10	0.2596 (3)	0.0469 (4)	0.5446 (3)	0.044 (1)	
C11	0.3242 (3)	0.1518 (5)	0.5843 (2)	0.042 (1)	
C12	0.3174 (3)	0.2147 (5)	0.6597 (3)	0.045 (1)	
C13	0.4183 (4)	0.0306 (6)	0.3148 (3)	0.076 (2)	
C14	0.1350 (3)	−0.1571 (5)	0.4654 (3)	0.061 (1)	
HC1	0.5453	0.5182	0.6392	0.055	
H1C4	0.3577	0.3110	0.8132	0.054	
H2C4	0.3207	0.4552	0.7640	0.054	
H1C5	0.4451	0.6135	0.7235	0.062	0.5
H2C5	0.5549	0.6135	0.7765	0.062	0.5
HC7	0.4605	0.1755	0.4404	0.042	
HC10	0.2068	0.0110	0.5717	0.044	
HC12	0.2646	0.1863	0.6889	0.045	
H1C13	0.4120	−0.0191	0.2609	0.076	
H2C13	0.4118	0.1340	0.3051	0.076	
H3C13	0.4827	0.0098	0.3492	0.076	
H1C14	0.0972	−0.2287	0.4287	0.061	
H2C14	0.1634	−0.2014	0.5193	0.061	
H3C14	0.0917	−0.0783	0.4748	0.061	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.058 (2)	0.066 (2)	0.055 (2)	−0.016 (2)	0.018 (2)	−0.021 (2)
O2	0.050 (2)	0.057 (2)	0.060 (2)	−0.014 (2)	0.007 (2)	0.003 (2)
N1	0.049 (2)	0.050 (3)	0.040 (2)	−0.007 (2)	0.000 (2)	0.002 (2)
C1	0.067 (3)	0.050 (3)	0.044 (3)	−0.007 (3)	0.000 (3)	0.004 (3)
C2	0.049 (3)	0.039 (3)	0.040 (3)	0.005 (2)	0.001 (2)	0.004 (3)
C3	0.046 (3)	0.047 (3)	0.039 (3)	0.009 (2)	0.001 (2)	0.007 (2)

C4	0.060 (3)	0.060 (3)	0.039 (3)	0.020 (3)	−0.001 (2)	−0.006 (3)
C5	0.089 (6)	0.045 (5)	0.048 (4)	0.0000	−0.002 (4)	0.0000
C6	0.039 (3)	0.044 (3)	0.038 (3)	0.006 (2)	0.002 (2)	0.007 (2)
C7	0.036 (3)	0.054 (3)	0.039 (3)	−0.006 (2)	0.010 (2)	−0.003 (3)
C8	0.042 (3)	0.045 (3)	0.040 (3)	0.006 (2)	0.007 (2)	0.002 (3)
C9	0.036 (3)	0.041 (3)	0.047 (3)	−0.006 (2)	0.001 (2)	0.001 (3)
C10	0.038 (3)	0.043 (3)	0.051 (3)	−0.003 (2)	0.006 (2)	0.006 (2)
C11	0.042 (3)	0.044 (3)	0.040 (3)	0.006 (3)	0.007 (2)	0.013 (3)
C12	0.043 (3)	0.054 (3)	0.038 (3)	0.006 (3)	0.007 (2)	0.012 (2)
C13	0.074 (4)	0.106 (5)	0.056 (3)	−0.032 (3)	0.029 (3)	−0.029 (3)
C14	0.050 (3)	0.060 (3)	0.072 (3)	−0.017 (3)	0.004 (3)	0.008 (3)

Geometric parameters (Å, °)

O1—C8	1.365 (4)	C6—C7	1.406 (5)
O1—C13	1.421 (5)	C6—C11	1.407 (5)
O2—C9	1.375 (5)	C7—C8	1.369 (5)
O2—C14	1.434 (4)	C7—HC7	1.000
N1—C2	1.328 (5)	C8—C9	1.406 (5)
N1—C6	1.371 (5)	C9—C10	1.352 (5)
C1—C2	1.510 (6)	C10—C11	1.428 (5)
C1—C4^{i}	1.545 (6)	C10—HC10	1.000
C1—C5	1.532 (5)	C11—C12	1.405 (5)
C1—HC1	1.000	C12—HC12	1.000
C2—C3	1.405 (5)	C13—H1C13	1.000
C3—C4	1.520 (5)	C13—H2C13	1.000
C3—C12	1.368 (5)	C13—H3C13	1.000
C4—H1C4	1.000	C14—H1C14	1.000
C4—H2C4	1.000	C14—H2C14	1.000
C5—H1C5	1.000	C14—H3C14	1.000
C5—H2C5	1.000		
C8—O1—C13	116.3 (4)	C6—C7—C8	120.1 (4)
C9—O2—C14	116.5 (3)	C6—C7—HC7	119.9
C2—N1—C6	117.9 (4)	C8—C7—HC7	119.9
C2—C1—C4^{i}	111.0 (4)	O1—C8—C7	125.1 (4)
C2—C1—C5	111.9 (4)	O1—C8—C9	114.9 (4)
C2—C1—HC1	108.6	C7—C8—C9	120.0 (4)
C4^{i}—C1—C5	108.3 (3)	O2—C9—C8	114.4 (4)
C4^{i}—C1—HC1	108.6	O2—C9—C10	124.3 (4)
C5—C1—HC1	108.6	C8—C9—C10	121.3 (4)
N1—C2—C1	114.8 (4)	C9—C10—C11	120.0 (4)
N1—C2—C3	123.6 (4)	C9—C10—HC10	120.0
C1—C2—C3	121.6 (4)	C11—C10—HC10	120.0
C2—C3—C4	121.3 (4)	C6—C11—C10	118.5 (4)
C2—C3—C12	118.2 (4)	C6—C11—C12	117.2 (4)
C4—C3—C12	120.5 (4)	C10—C11—C12	124.3 (4)
C1^{i}—C4—C3	111.8 (4)	C3—C12—C11	120.7 (4)
C1^{i}—C4—H1C4	108.9	C3—C12—HC12	119.7

C1^{i}—C4—H2C4	108.9	C11—C12—HC12	119.7
C3—C4—H1C4	108.9	O1—C13—H1C13	109.5
C3—C4—H2C4	108.9	O1—C13—H2C13	109.5
H1C4—C4—H2C4	109.5	O1—C13—H3C13	109.5
C1—C5—C1^{i}	107.7 (5)	H1C13—C13—H2C13	109.5
C1—C5—H1C5	109.9	H1C13—C13—H3C13	109.5
C1—C5—H2C5	109.9	H2C13—C13—H3C13	109.5
C1^{i}—C5—H1C5	109.9	O2—C14—H1C14	109.5
C1^{i}—C5—H2C5	109.9	O2—C14—H2C14	109.5
H1C5—C5—H2C5	109.5	O2—C14—H3C14	109.5
N1—C6—C7	117.5 (4)	H1C14—C14—H2C14	109.5
N1—C6—C11	122.5 (4)	H1C14—C14—H3C14	109.5
C7—C6—C11	120.0 (4)	H2C14—C14—H3C14	109.5

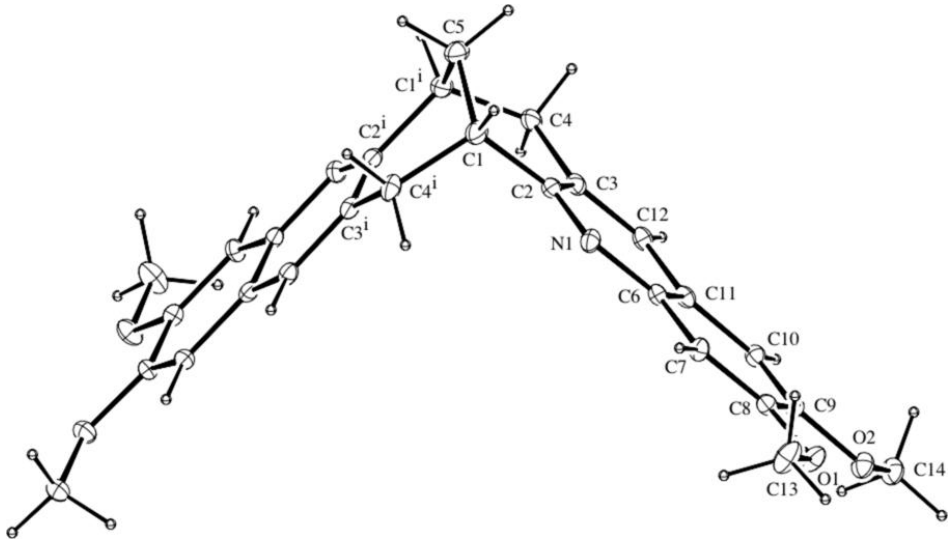
Symmetry codes: (i) −*x*+1, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H3C14···N1^{ii}	1.00	2.882	3.723 (5)	142
C14—H3C14···N1^{iii}	1.00	2.958	3.348 (5)	104

Symmetry codes: (ii) −*x*+1/2, −*y*+1/2, −*z*+1; (iii) *x*−1/2, *y*−1/2, *z*.

Fig. 1


C5
C1i
C2i
C4
C1
C4i
C2
C3
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C13
O1

Fig. 2

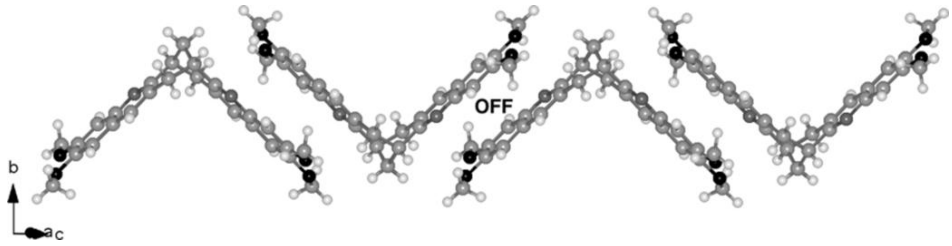

Fig. 3