Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,3,8,12,13-Pentamethoxy-5*H*-dibenzo[*c*,*n*]acridin-7(6*H*)-one toluene solvate

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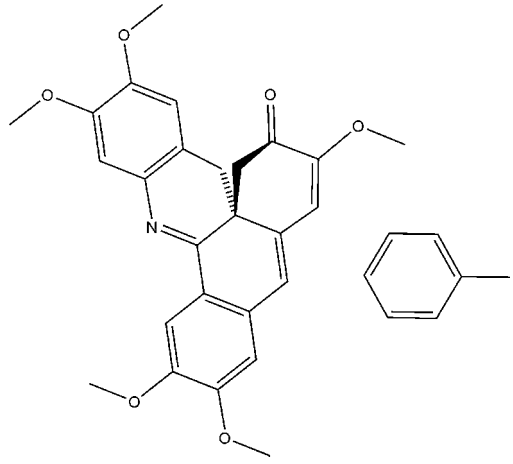
Received 13 August 2007; accepted 15 August 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.076; wR factor = 0.199; data-to-parameter ratio = 28.9.

The title compound, $C_{26}H_{25}NO_6\cdot C_7H_8$, formed by an unexpected tandem reaction of Beckmann rearrangement, electrophilic aromatic addition and subsequent demethylation, was crystallized as its toluene solvate. The crystal under investigation was found to be nonmerohedrally twinned by a rotation around the reciprocal axis [100]; the twin ratio refined to 0.688 (2):0.312 (2). The molecule exhibits an unusual helical arrangement of three six-membered rings that are all connected at one central C atom. The helix effectively performs one full turn around this atom, and the thread pitch, as defined by the distance of the terminal C atoms of the helix, is 4.98 (3) Å. The angles around the central atom are between 104.7 (2) and 115.2 (2)°. The middle ring, a cyclohexa-2,4-dienimine ring containing only one saturated C atom, is essentially planar, with an r.m.s. deviation from the mean plane of only 0.035 Å. The other two rings have conformations best described as between envelope and screw-boat, with puckering amplitudes of 0.527 (2) and 0.544 (2) Å, respectively. The packing appears to be dominated by a combination of simple dispersion forces, weak C—H···O hydrogen bonds and C—H···π interactions.

Related literature

For the use of crown-shaped [1.1.1]orthocyclophane cyclotriveratrylene (CTV, hexamethoxytribenzocyclononene) as a scaffold in supramolecular chemistry, see: Collet (1987). For crown and saddle conformers of CTV oxime, see: Lutz *et al.* (2007). For other related literature, see: Boeyens (1978); Cremer & Pople (1975); Herbstein (2000).



Experimental

Crystal data

$C_{26}H_{25}NO_6\cdot C_7H_8$
M_r = 539.60
Monoclinic, $P2_1/c$
a = 14.952 (4) Å
b = 7.1736 (18) Å
c = 25.787 (6) Å
β = 94.571 (7)°
V = 2757.1 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 (2) K
0.60 × 0.19 × 0.09 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*TWINABS*; Bruker, 2003)
T_{min} = 0.773, T_{max} = 1.000
(expected range = 0.767–0.992)
40178 measured reflections
10641 independent reflections
7887 reflections with $I > 2\sigma(I)$
R_{int} not defined due to twin pairing errors (Herbst-Irmer, 2006)

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.199
S = 1.08
10641 reflections
368 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Hydrogen bonding and C—H···π interactions.

*Cg*1 denotes the centroid of ring C8–C13, *Cg*2 that of C15–C20 and *Cg*3 that of C27–C32.

D—H···A	D—H	H···A	D···A	D—H···A
C23—H23*B*···O4^{i}	0.98	2.41	3.354 (3)	160.4
C26—H26*B*···O2^{ii}	0.98	2.59	3.210 (3)	120.9
C26—H26*C*···O6^{iii}	0.98	2.58	3.526 (3)	162.2
C12—H12···*Cg*2^{iv}	0.95	3.32	3.780 (2)	112
C22—H22*A*···*Cg*2^{iii}	0.98	2.97	3.557 (3)	120
C23—H23*C*···*Cg*1^{v}	0.98	2.99	3.902 (3)	156
C24—H24*A*···*Cg*3^{vi}	0.98	2.66	3.447 (3)	137
C25—H25*C*···*Cg*3	0.98	2.63	3.487 (3)	146

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *CELL_NOW* (Sheldrick, 2004) and *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

 doi:10.1107/S1600536807040548

The diffractometer was funded by NSF grant 0087210, by Ohio Board of Regents grant CAP-491 and by Youngstown State University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2480).

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supplementary materials

Acta Cryst. (2007). E**63**, o3857-o3858 [**doi:10.1107/S1600536807040548**]

2,3,8,12,13-Pentamethoxy-5*H*-dibenzo[*c*,*n*]acridin-7(6*H*)-one toluene solvate

M. R. Lutz Jr, M. Zeller and D. P. Becker

Comment

The crown-shaped [1.1.1]orthocyclophane cyclotriveratrylene (CTV, hexamethoxy tribenzocyclononene) molecule has been employed extensively as a scaffold in supramolecular chemistry (Collet, 1987). We are interested in new apex-modified derivatives of CTV and recently reported the isolation of the crown and saddle conformers of CTV oxime (Lutz *et al.*, 2007). In the course of studying the Beckmann rearrangement of this molecule we observed the unexpected formation of the title compound, resulting from a Beckmann rearrangement followed by an intramolecular electrophilic aromatic addition and subsequent demethylation (Fig. 1). Studies of the reaction conditions and mechanism will be discussed in detail in a separate publication.

The title compound was crystallized from methylene chloride/toluene as its toluene solvate (Figure 2). The red needle-like crystals were heavily intergrown, and the crystal that was finally selected for single-crystal data collection was found to be non-merohedrally twinned with two twin components in a ratio of 0.688 (2) to 0.312 (2) (See experimental refinement section for details of unit cell determination, data workup, refinement, and type of twinning).

The compound shows an unusual helical arrangement of three six-membered rings that are all connected at the central carbon atom C6. The helix effectively performs one full turn around C6, and the thread pitch, as defined by the distance of the terminal atoms C2 and C20 of the helix, is 4.98 (3) Å. The angles around C6 are between 104.7 (2) and 115.2 (2)°. The middle ring, a cyclohexa-2,4-dienimine with C6 being the only saturated atom in the ring, is nearly planar with an r.m.s. deviation from the mean plane of only 0.035 Å. The other two rings have conformations best described as between envelope and screw-boat (Boeyens, 1978) with puckering amplitudes of 0.527 (2) and 0.544 (2) Å, respectively (Cremer & Pople, 1975).

The packing of the title compound, illustrated in Figure 3, seems to be dominated by a combination of simple dispersion forces, and weak interactions of the methoxy methyl hydrogen bonds with both neigboring oxygen atoms and aromatic rings. All methoxy groups are involved in at least one C—H···O hydrogen bond or C—H···π contact, and all aromatic rings act as an acceptor to one or two methoxy CH_3 groups.

Experimental

To a solution of the crown conformer of CTV oxime (10,15-dihydro-2,3,7,8,12,13-hexamethoxy-5*H*-tribenzo[a,d,g]cyclononen-5-oxime, 200 mg, 0.417 mmol) in 4 ml diethyl ether and 1 ml of dichloromethane at 273 K was added thionyl chloride (1.88 g, 15.8 mmol) dropwise over 1 minute. The reaction mixture was stirred for 5 minutes at 273 K, then poured over ice and extracted with methylene chloride. The organic layer was washed successively with saturated aqueous sodium bicarbonate, water and brine, and then dried over sodium sulfate. Concentration gave a residue which was chromatographed on silica gel eluting with ethyl acetate/methylene chloride (30/70) to afford 0.028 g of a solid which was recrystallized from toluene/dichloromethane to give 0.023 g (23%) of the product as red-bronze crystals.

Refinement

The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now (Sheldrick, 2004), and the two components were integrated using Saint+ (Bruker, 2003), resulting in a total of 40178 reflections. 12959 reflections (5474 unique) involved component 1 only (mean I/sigma = 5.5), 12616 reflections (5374 unique ones) involved component 2 only (mean I/sigma = 3.7), and 14603 reflections (7998 unique ones) involved both components (mean I/sigma = 6.4). The exact twin matrix identified by the integration program was found to be 0.99876 − 0.00396 − 0.00012, 0.00212 0.99889 0.00875, −0.00309 − 0.11163 0.99795, which is for this structure equivalent to a 180° rotation around the reciprocal axis [1 0 0].

The data were corrected for absorption using Twinabs (Bruker, 2003), and the structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones) below a *d*-spacing threshold of 3/4, resulting in a BASF value of 0.312 (2). Due to "twin pairing errors" in Saint+ (equivalent reflections being counted as overlapping for one reflection, but as not overlapping for an eqivalent one) no accurate R_{int} value can be given. This also results in an incomplete merging of equivalent reflections in Twinabs, thus resulting in too many independent reflections. (Herbst-Irmer, 2006)

Hydrogen atoms were added in calculated positions with C—H distances of 0.95, 0.99 and 0.98 Å for aromatic, methylene and methyl H atoms, respectively, and were refined with $U_{iso}(H) = x\ U_{eq}(C)$ (x = 1.2 for C—H and CH_2, 1.5 for CH_3).

The s.u. values of the cell parameters are taken from the software recognizing that the values are unreasonably small (Herbstein, 2000).

Figures

Fig. 1. Synthesis of the title compound.

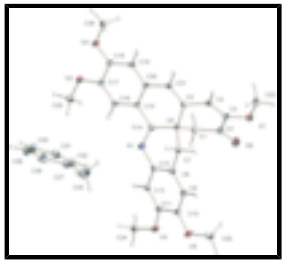

Fig. 2. The molecular structure of the title compound with the atomic numbering scheme. Thermal displacement parameters are at the 50% probabilty level.

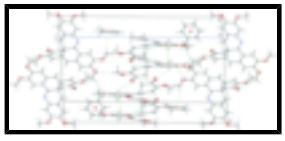

Fig. 3. Partially expanded packing diagram of the title compound with 50% probability thermal ellipsoids. C—H···O hydrogen bonds are indicated by broken turquoise lines, C—H···π contacts by dashed blue lines.

2,3,8,12,13-Pentamethoxy-5*H*-dibenzo[c,n]acridin-7(6*H*)-one toluene solvate

Crystal data

$C_{26}H_{25}NO_6 \cdot C_7H_8$	$F_{000} = 1144$
$M_r = 539.60$	$D_x = 1.300$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 6322 reflections
$a = 14.952$ (4) Å	$\theta = 3.0$–$30.5°$
$b = 7.1736$ (18) Å	$\mu = 0.09$ mm^{-1}
$c = 25.787$ (6) Å	$T = 100$ (2) K
$\beta = 94.571$ (7)°	Rod, red
$V = 2757.1$ (12) Å^3	0.60 × 0.19 × 0.09 mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD diffractometer	10641 independent reflections
Radiation source: fine-focus sealed tube	7887 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = not defined due to twin pairing errors, Herbst-Irmer, 2006
$T = 100(2)$ K	$\theta_{max} = 28.3°$
ω scans	$\theta_{min} = 1.4°$
Absorption correction: multi-scan (TWINABS; Bruker, 2003)	$h = -19 \rightarrow 19$
$T_{min} = 0.773$, $T_{max} = 1.000$	$k = 0 \rightarrow 9$
40178 measured reflections	$l = 0 \rightarrow 34$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.076$	H-atom parameters constrained
$wR(F^2) = 0.199$	$w = 1/[\sigma^2(F_o^2) + (0.0913P)^2 + 1.3281P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
10641 reflections	$\Delta\rho_{max} = 0.67$ e Å^{-3}
368 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, and the two components were integrated using Saint, resulting in a total of 40178 reflections. 12959 reflections (5474 unique ones) involved component 1 only (mean I/sigma = 5.5), 12616 reflections (5374 unique ones) involved component 2 only (mean I/sigma = 3.7), and 14603 reflections (7998 unique ones) involved both components (mean I/sigma = 6.4). The exact twin matrix identified by the integration program was found to be 0.99876 − 0.00396 − 0.00012, 0.00212 0.99889 0.00875, −0.00309 − 0.11163 0.99795.

The data were corrected for absorption using twinabs, and the structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones) below a *d*-spacing threshold of 3/4, resulting in a BASF value of 0.312 (2).

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.36910 (14)	0.6758 (3)	0.48902 (8)	0.0190 (4)
H1A	0.3447	0.5551	0.4757	0.023*
H1B	0.4282	0.6947	0.4751	0.023*
C2	0.38116 (14)	0.6689 (3)	0.54776 (8)	0.0202 (4)
C3	0.38050 (14)	0.8509 (3)	0.57581 (8)	0.0193 (4)
C4	0.36991 (14)	1.0121 (3)	0.54819 (8)	0.0192 (4)
H4	0.3771	1.1280	0.5659	0.023*
C5	0.34790 (13)	1.0112 (3)	0.49225 (7)	0.0164 (4)
C6	0.30468 (14)	0.8353 (3)	0.46952 (7)	0.0161 (4)
C7	0.21107 (14)	0.7989 (3)	0.48916 (8)	0.0175 (4)
H7A	0.2157	0.7918	0.5276	0.021*
H7B	0.1696	0.9016	0.4782	0.021*
C8	0.17650 (14)	0.6175 (3)	0.46620 (8)	0.0174 (4)
C9	0.12927 (14)	0.4885 (3)	0.49419 (8)	0.0193 (4)
H9	0.1164	0.5165	0.5288	0.023*
C10	0.10097 (14)	0.3203 (3)	0.47201 (8)	0.0191 (4)
C11	0.11910 (14)	0.2807 (3)	0.42046 (8)	0.0183 (4)
C12	0.16534 (13)	0.4081 (3)	0.39220 (7)	0.0169 (4)
H12	0.1769	0.3814	0.3573	0.020*
C13	0.19494 (13)	0.5765 (3)	0.41539 (7)	0.0165 (4)
C14	0.28966 (13)	0.8315 (3)	0.40988 (7)	0.0156 (4)
C15	0.32871 (13)	0.9817 (3)	0.37944 (7)	0.0159 (4)
C16	0.32393 (13)	0.9731 (3)	0.32478 (7)	0.0159 (4)

H16	0.2972	0.8679	0.3074	0.019*
C17	0.35782 (13)	1.1168 (3)	0.29594 (8)	0.0160 (4)
C18	0.39549 (13)	1.2758 (3)	0.32219 (8)	0.0167 (4)
C19	0.39815 (13)	1.2865 (3)	0.37567 (8)	0.0172 (4)
H19	0.4221	1.3948	0.3929	0.021*
C20	0.36590 (13)	1.1392 (3)	0.40523 (8)	0.0156 (4)
C21	0.37340 (14)	1.1502 (3)	0.46147 (8)	0.0180 (4)
H21	0.3974	1.2606	0.4774	0.022*
C22	0.41041 (17)	1.0041 (3)	0.65651 (8)	0.0256 (5)
H22A	0.4633	1.0682	0.6452	0.038*
H22B	0.4197	0.9764	0.6938	0.038*
H22C	0.3576	1.0843	0.6501	0.038*
C23	0.05158 (16)	0.2025 (3)	0.55146 (8)	0.0254 (5)
H23A	0.1125	0.2149	0.5681	0.038*
H23B	0.0231	0.0913	0.5649	0.038*
H23C	0.0164	0.3131	0.5590	0.038*
C24	0.09328 (15)	0.0706 (3)	0.34878 (8)	0.0221 (5)
H24A	0.0601	0.1665	0.3281	0.033*
H24B	0.0664	−0.0517	0.3408	0.033*
H24C	0.1560	0.0701	0.3403	0.033*
C25	0.32396 (16)	0.9605 (3)	0.21512 (8)	0.0251 (5)
H25A	0.3573	0.8492	0.2274	0.038*
H25B	0.3303	0.9779	0.1779	0.038*
H25C	0.2604	0.9451	0.2208	0.038*
C26	0.46204 (15)	1.5756 (3)	0.31657 (8)	0.0209 (5)
H26A	0.4142	1.6355	0.3344	0.031*
H26B	0.4837	1.6616	0.2908	0.031*
H26C	0.5116	1.5426	0.3421	0.031*
C27	0.14872 (15)	0.6018 (3)	0.21337 (8)	0.0239 (5)
C28	0.14841 (16)	0.6401 (4)	0.16066 (9)	0.0299 (6)
H28	0.1748	0.5535	0.1385	0.036*
C29	0.11040 (18)	0.8023 (4)	0.13957 (9)	0.0365 (6)
H29	0.1103	0.8252	0.1033	0.044*
C30	0.07272 (17)	0.9308 (4)	0.17138 (10)	0.0335 (6)
H30	0.0471	1.0426	0.1571	0.040*
C31	0.07257 (16)	0.8953 (3)	0.22406 (9)	0.0271 (5)
H31	0.0467	0.9829	0.2461	0.033*
C32	0.11011 (15)	0.7325 (3)	0.24480 (8)	0.0233 (5)
H32	0.1095	0.7094	0.2810	0.028*
C33	0.18935 (19)	0.4249 (4)	0.23630 (10)	0.0384 (6)
H33A	0.2126	0.3497	0.2086	0.058*
H33B	0.1434	0.3541	0.2529	0.058*
H33C	0.2385	0.4561	0.2623	0.058*
N1	0.24151 (11)	0.7050 (2)	0.38542 (6)	0.0174 (4)
O1	0.39663 (10)	0.8337 (2)	0.62800 (5)	0.0222 (3)
O2	0.35886 (10)	1.1202 (2)	0.24319 (5)	0.0203 (3)
O3	0.42770 (10)	1.4094 (2)	0.29075 (5)	0.0210 (3)
O4	0.08931 (10)	0.1096 (2)	0.40264 (5)	0.0222 (3)
O5	0.05546 (10)	0.1852 (2)	0.49660 (5)	0.0239 (4)

O6	0.39527 (12)	0.5216 (2)	0.57117 (6)	0.0308 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0221 (11)	0.0138 (10)	0.0210 (10)	0.0001 (9)	0.0014 (8)	−0.0018 (8)
C2	0.0192 (11)	0.0185 (11)	0.0225 (11)	−0.0013 (9)	−0.0014 (8)	0.0001 (8)
C3	0.0202 (11)	0.0192 (11)	0.0184 (10)	−0.0038 (9)	0.0018 (8)	−0.0013 (8)
C4	0.0223 (11)	0.0151 (10)	0.0204 (10)	−0.0038 (9)	0.0031 (8)	−0.0028 (8)
C5	0.0171 (10)	0.0131 (10)	0.0193 (10)	−0.0005 (8)	0.0027 (8)	−0.0030 (8)
C6	0.0193 (10)	0.0131 (10)	0.0160 (9)	−0.0019 (9)	0.0018 (8)	0.0002 (7)
C7	0.0206 (10)	0.0148 (10)	0.0176 (10)	−0.0014 (9)	0.0043 (8)	−0.0029 (8)
C8	0.0168 (10)	0.0150 (10)	0.0203 (10)	0.0002 (9)	0.0017 (8)	−0.0009 (8)
C9	0.0238 (11)	0.0180 (10)	0.0167 (10)	−0.0026 (9)	0.0065 (8)	−0.0021 (8)
C10	0.0201 (10)	0.0166 (10)	0.0207 (10)	−0.0026 (9)	0.0027 (8)	0.0034 (8)
C11	0.0195 (10)	0.0128 (10)	0.0224 (10)	−0.0032 (9)	−0.0002 (8)	0.0000 (8)
C12	0.0187 (10)	0.0166 (10)	0.0156 (9)	−0.0003 (9)	0.0023 (8)	0.0009 (8)
C13	0.0163 (10)	0.0148 (10)	0.0182 (10)	−0.0013 (9)	−0.0009 (8)	0.0027 (8)
C14	0.0160 (10)	0.0123 (10)	0.0187 (10)	0.0019 (8)	0.0019 (8)	−0.0021 (8)
C15	0.0144 (10)	0.0141 (10)	0.0195 (10)	−0.0004 (8)	0.0026 (7)	0.0020 (8)
C16	0.0145 (9)	0.0126 (10)	0.0207 (10)	−0.0009 (8)	0.0019 (8)	−0.0002 (8)
C17	0.0138 (10)	0.0160 (10)	0.0182 (9)	0.0013 (8)	0.0024 (7)	−0.0001 (8)
C18	0.0143 (10)	0.0144 (10)	0.0214 (10)	−0.0003 (8)	0.0025 (8)	0.0022 (8)
C19	0.0161 (10)	0.0110 (9)	0.0245 (10)	−0.0013 (8)	0.0011 (8)	0.0005 (8)
C20	0.0145 (10)	0.0113 (9)	0.0212 (10)	−0.0003 (8)	0.0022 (8)	0.0007 (7)
C21	0.0206 (10)	0.0134 (10)	0.0200 (10)	−0.0023 (9)	0.0022 (8)	−0.0018 (8)
C22	0.0352 (13)	0.0216 (11)	0.0198 (11)	−0.0029 (11)	0.0004 (9)	−0.0048 (9)
C23	0.0306 (12)	0.0254 (12)	0.0206 (11)	−0.0101 (10)	0.0048 (9)	0.0028 (9)
C24	0.0235 (11)	0.0203 (11)	0.0226 (11)	−0.0030 (10)	0.0022 (8)	−0.0042 (8)
C25	0.0303 (13)	0.0249 (12)	0.0203 (11)	−0.0060 (10)	0.0025 (9)	−0.0032 (9)
C26	0.0236 (11)	0.0143 (10)	0.0252 (11)	−0.0039 (9)	0.0048 (9)	0.0007 (8)
C27	0.0211 (11)	0.0230 (12)	0.0275 (12)	−0.0040 (10)	0.0018 (9)	−0.0001 (9)
C28	0.0273 (13)	0.0334 (14)	0.0301 (12)	−0.0003 (11)	0.0088 (10)	−0.0058 (10)
C29	0.0406 (15)	0.0467 (16)	0.0224 (12)	−0.0016 (13)	0.0046 (10)	0.0100 (11)
C30	0.0327 (14)	0.0270 (13)	0.0403 (14)	0.0006 (12)	−0.0007 (11)	0.0076 (11)
C31	0.0268 (12)	0.0220 (12)	0.0323 (12)	0.0001 (10)	0.0013 (10)	−0.0058 (10)
C32	0.0235 (11)	0.0270 (12)	0.0194 (10)	−0.0029 (10)	0.0023 (8)	−0.0010 (9)
C33	0.0398 (15)	0.0315 (14)	0.0447 (15)	0.0056 (13)	0.0085 (12)	0.0043 (12)
N1	0.0189 (9)	0.0140 (9)	0.0198 (9)	−0.0025 (7)	0.0038 (7)	0.0005 (7)
O1	0.0296 (8)	0.0186 (8)	0.0180 (7)	−0.0058 (7)	0.0000 (6)	−0.0002 (6)
O2	0.0255 (8)	0.0187 (8)	0.0173 (7)	−0.0054 (7)	0.0050 (6)	−0.0007 (6)
O3	0.0257 (8)	0.0169 (8)	0.0210 (7)	−0.0071 (7)	0.0050 (6)	0.0016 (6)
O4	0.0301 (9)	0.0165 (8)	0.0204 (7)	−0.0082 (7)	0.0040 (6)	−0.0021 (6)
O5	0.0323 (9)	0.0193 (8)	0.0212 (7)	−0.0089 (7)	0.0085 (6)	0.0006 (6)
O6	0.0452 (11)	0.0174 (8)	0.0282 (9)	−0.0005 (8)	−0.0069 (7)	0.0044 (7)

Geometric parameters (Å, °)

C1—C2	1.512 (3)	C19—H19	0.9500

C1—C6	1.553 (3)	C20—C21	1.448 (3)
C1—H1A	0.9900	C21—H21	0.9500
C1—H1B	0.9900	C22—O1	1.433 (2)
C2—O6	1.227 (2)	C22—H22A	0.9800
C2—C3	1.493 (3)	C22—H22B	0.9800
C3—O1	1.354 (2)	C22—H22C	0.9800
C3—C4	1.361 (3)	C23—O5	1.426 (2)
C4—C5	1.454 (3)	C23—H23A	0.9800
C4—H4	0.9500	C23—H23B	0.9800
C5—C21	1.348 (3)	C23—H23C	0.9800
C5—C6	1.515 (3)	C24—O4	1.423 (2)
C6—C14	1.537 (3)	C24—H24A	0.9800
C6—C7	1.548 (3)	C24—H24B	0.9800
C7—C8	1.504 (3)	C24—H24C	0.9800
C7—H7A	0.9900	C25—O2	1.431 (2)
C7—H7B	0.9900	C25—H25A	0.9800
C8—C13	1.392 (3)	C25—H25B	0.9800
C8—C9	1.399 (3)	C25—H25C	0.9800
C9—C10	1.387 (3)	C26—O3	1.440 (2)
C9—H9	0.9500	C26—H26A	0.9800
C10—O5	1.369 (2)	C26—H26B	0.9800
C10—C11	1.407 (3)	C26—H26C	0.9800
C11—O4	1.372 (2)	C27—C28	1.386 (3)
C11—C12	1.387 (3)	C27—C32	1.394 (3)
C12—C13	1.404 (3)	C27—C33	1.507 (3)
C12—H12	0.9500	C28—C29	1.387 (3)
C13—N1	1.420 (2)	C28—H28	0.9500
C14—N1	1.291 (3)	C29—C30	1.383 (4)
C14—C15	1.480 (3)	C29—H29	0.9500
C15—C20	1.403 (3)	C30—C31	1.382 (3)
C15—C16	1.407 (3)	C30—H30	0.9500
C16—C17	1.390 (3)	C31—C32	1.385 (3)
C16—H16	0.9500	C31—H31	0.9500
C17—O2	1.362 (2)	C32—H32	0.9500
C17—C18	1.420 (3)	C33—H33A	0.9800
C18—O3	1.368 (2)	C33—H33B	0.9800
C18—C19	1.379 (3)	C33—H33C	0.9800
C19—C20	1.411 (3)		
C2—C1—C6	111.71 (16)	C15—C20—C19	119.14 (18)
C2—C1—H1A	109.3	C15—C20—C21	120.99 (18)
C6—C1—H1A	109.3	C19—C20—C21	119.86 (18)
C2—C1—H1B	109.3	C5—C21—C20	123.13 (19)
C6—C1—H1B	109.3	C5—C21—H21	118.4
H1A—C1—H1B	107.9	C20—C21—H21	118.4
O6—C2—C3	121.48 (19)	O1—C22—H22A	109.5
O6—C2—C1	121.57 (19)	O1—C22—H22B	109.5
C3—C2—C1	116.85 (18)	H22A—C22—H22B	109.5
O1—C3—C4	127.01 (19)	O1—C22—H22C	109.5
O1—C3—C2	113.21 (18)	H22A—C22—H22C	109.5

C4—C3—C2	119.65 (18)	H22B—C22—H22C	109.5
C3—C4—C5	121.56 (19)	O5—C23—H23A	109.5
C3—C4—H4	119.2	O5—C23—H23B	109.5
C5—C4—H4	119.2	H23A—C23—H23B	109.5
C21—C5—C4	121.93 (19)	O5—C23—H23C	109.5
C21—C5—C6	121.36 (17)	H23A—C23—H23C	109.5
C4—C5—C6	116.32 (17)	H23B—C23—H23C	109.5
C5—C6—C14	115.20 (16)	O4—C24—H24A	109.5
C5—C6—C7	112.52 (16)	O4—C24—H24B	109.5
C14—C6—C7	105.10 (16)	H24A—C24—H24B	109.5
C5—C6—C1	104.72 (16)	O4—C24—H24C	109.5
C14—C6—C1	110.39 (16)	H24A—C24—H24C	109.5
C7—C6—C1	108.88 (16)	H24B—C24—H24C	109.5
C8—C7—C6	107.96 (16)	O2—C25—H25A	109.5
C8—C7—H7A	110.1	O2—C25—H25B	109.5
C6—C7—H7A	110.1	H25A—C25—H25B	109.5
C8—C7—H7B	110.1	O2—C25—H25C	109.5
C6—C7—H7B	110.1	H25A—C25—H25C	109.5
H7A—C7—H7B	108.4	H25B—C25—H25C	109.5
C13—C8—C9	119.48 (19)	O3—C26—H26A	109.5
C13—C8—C7	117.74 (18)	O3—C26—H26B	109.5
C9—C8—C7	122.76 (17)	H26A—C26—H26B	109.5
C10—C9—C8	120.85 (18)	O3—C26—H26C	109.5
C10—C9—H9	119.6	H26A—C26—H26C	109.5
C8—C9—H9	119.6	H26B—C26—H26C	109.5
O5—C10—C9	124.88 (18)	C28—C27—C32	117.9 (2)
O5—C10—C11	115.76 (18)	C28—C27—C33	121.4 (2)
C9—C10—C11	119.36 (18)	C32—C27—C33	120.7 (2)
O4—C11—C12	125.11 (18)	C27—C28—C29	121.3 (2)
O4—C11—C10	114.56 (17)	C27—C28—H28	119.3
C12—C11—C10	120.31 (19)	C29—C28—H28	119.3
C11—C12—C13	119.77 (18)	C30—C29—C28	120.0 (2)
C11—C12—H12	120.1	C30—C29—H29	120.0
C13—C12—H12	120.1	C28—C29—H29	120.0
C8—C13—C12	120.21 (18)	C31—C30—C29	119.5 (2)
C8—C13—N1	121.20 (18)	C31—C30—H30	120.2
C12—C13—N1	118.56 (17)	C29—C30—H30	120.2
N1—C14—C15	118.74 (17)	C30—C31—C32	120.2 (2)
N1—C14—C6	122.18 (18)	C30—C31—H31	119.9
C15—C14—C6	119.04 (17)	C32—C31—H31	119.9
C20—C15—C16	119.78 (18)	C31—C32—C27	121.1 (2)
C20—C15—C14	119.54 (17)	C31—C32—H32	119.5
C16—C15—C14	120.57 (18)	C27—C32—H32	119.5
C17—C16—C15	120.79 (18)	C27—C33—H33A	109.5
C17—C16—H16	119.6	C27—C33—H33B	109.5
C15—C16—H16	119.6	H33A—C33—H33B	109.5
O2—C17—C16	125.53 (18)	C27—C33—H33C	109.5
O2—C17—C18	115.24 (17)	H33A—C33—H33C	109.5
C16—C17—C18	119.23 (18)	H33B—C33—H33C	109.5

O3—C18—C19	124.78 (18)	C14—N1—C13	117.94 (17)
O3—C18—C17	115.18 (17)	C3—O1—C22	116.05 (16)
C19—C18—C17	120.04 (18)	C17—O2—C25	117.29 (15)
C18—C19—C20	120.98 (19)	C18—O3—C26	115.81 (15)
C18—C19—H19	119.5	C11—O4—C24	117.74 (16)
C20—C19—H19	119.5	C10—O5—C23	117.31 (16)
C6—C1—C2—O6	148.9 (2)	N1—C14—C15—C20	167.52 (18)
C6—C1—C2—C3	−34.6 (3)	C6—C14—C15—C20	−10.2 (3)
O6—C2—C3—O1	−0.1 (3)	N1—C14—C15—C16	−8.6 (3)
C1—C2—C3—O1	−176.55 (17)	C6—C14—C15—C16	173.70 (18)
O6—C2—C3—C4	176.1 (2)	C20—C15—C16—C17	1.7 (3)
C1—C2—C3—C4	−0.4 (3)	C14—C15—C16—C17	177.83 (18)
O1—C3—C4—C5	−176.57 (19)	C15—C16—C17—O2	178.08 (18)
C2—C3—C4—C5	7.9 (3)	C15—C16—C17—C18	−1.6 (3)
C3—C4—C5—C21	−151.1 (2)	O2—C17—C18—O3	−0.2 (3)
C3—C4—C5—C6	21.7 (3)	C16—C17—C18—O3	179.55 (18)
C21—C5—C6—C14	−2.0 (3)	O2—C17—C18—C19	−179.77 (18)
C4—C5—C6—C14	−174.90 (17)	C16—C17—C18—C19	0.0 (3)
C21—C5—C6—C7	−122.5 (2)	O3—C18—C19—C20	−177.93 (18)
C4—C5—C6—C7	64.6 (2)	C17—C18—C19—C20	1.6 (3)
C21—C5—C6—C1	119.4 (2)	C16—C15—C20—C19	−0.1 (3)
C4—C5—C6—C1	−53.5 (2)	C14—C15—C20—C19	−176.29 (18)
C2—C1—C6—C5	58.7 (2)	C16—C15—C20—C21	−178.69 (19)
C2—C1—C6—C14	−176.78 (17)	C14—C15—C20—C21	5.1 (3)
C2—C1—C6—C7	−61.9 (2)	C18—C19—C20—C15	−1.5 (3)
C5—C6—C7—C8	−177.45 (16)	C18—C19—C20—C21	177.05 (19)
C14—C6—C7—C8	56.4 (2)	C4—C5—C21—C20	169.34 (19)
C1—C6—C7—C8	−61.8 (2)	C6—C5—C21—C20	−3.2 (3)
C6—C7—C8—C13	−37.5 (2)	C15—C20—C21—C5	1.7 (3)
C6—C7—C8—C9	140.8 (2)	C19—C20—C21—C5	−176.8 (2)
C13—C8—C9—C10	0.2 (3)	C32—C27—C28—C29	−0.5 (3)
C7—C8—C9—C10	−178.02 (19)	C33—C27—C28—C29	179.5 (2)
C8—C9—C10—O5	179.2 (2)	C27—C28—C29—C30	0.7 (4)
C8—C9—C10—C11	−0.9 (3)	C28—C29—C30—C31	−0.6 (4)
O5—C10—C11—O4	−0.9 (3)	C29—C30—C31—C32	0.2 (4)
C9—C10—C11—O4	179.11 (18)	C30—C31—C32—C27	0.1 (3)
O5—C10—C11—C12	−179.63 (18)	C28—C27—C32—C31	0.0 (3)
C9—C10—C11—C12	0.4 (3)	C33—C27—C32—C31	−180.0 (2)
O4—C11—C12—C13	−177.92 (19)	C15—C14—N1—C13	−171.83 (17)
C10—C11—C12—C13	0.7 (3)	C6—C14—N1—C13	5.8 (3)
C9—C8—C13—C12	0.8 (3)	C8—C13—N1—C14	20.8 (3)
C7—C8—C13—C12	179.18 (18)	C12—C13—N1—C14	−160.95 (18)
C9—C8—C13—N1	179.03 (19)	C4—C3—O1—C22	−4.9 (3)
C7—C8—C13—N1	−2.6 (3)	C2—C3—O1—C22	170.91 (18)
C11—C12—C13—C8	−1.3 (3)	C16—C17—O2—C25	−1.5 (3)
C11—C12—C13—N1	−179.52 (18)	C18—C17—O2—C25	178.24 (17)
C5—C6—C14—N1	−169.12 (18)	C19—C18—O3—C26	−3.4 (3)
C7—C6—C14—N1	−44.7 (2)	C17—C18—O3—C26	177.01 (17)
C1—C6—C14—N1	72.6 (2)	C12—C11—O4—C24	−10.4 (3)

C5—C6—C14—C15	8.5 (3)	C10—C11—O4—C24	170.96 (18)
C7—C6—C14—C15	132.91 (18)	C9—C10—O5—C23	−12.3 (3)
C1—C6—C14—C15	−109.8 (2)	C11—C10—O5—C23	167.70 (19)

Table 1. Hydrogen bonding and C-H···π interactions

D—H···A	D—H	H···A	D···A	D—H···A
C23—H23B···O4^{i}	0.98	2.41	3.354 (3)	160.4
C26—H26B···O2^{ii}	0.98	2.59	3.210 (3)	120.9
C26—H26C···O6^{iii}	0.98	2.58	3.526 (3)	162.2
C12—H12···*Cg*2^{iV}	0.95	3.3199	3.780 (2)	112.02
C22—H22A···*Cg*2^{iii}	0.98	2.9687	3.557 (3)	119.73
C23—H23C···*Cg*1^{v}	0.98	2.9869	3.902 (3)	155.82
C24—H24A···*Cg*3^{vi}	0.98	2.6627	3.447 (3)	137.12
C25—H25C···*Cg*3	0.98	2.6327	3.487 (3)	145.87

*Cg*1 denotes the centroid of ring C8–C13, *Cg*2 that of C15–C20, and *Cg*3 that of C27–C32. Symmetry codes: (i) −*x*, −*y*, −*z* + 1; (ii) −*x* + 1, *y* + 1/2, −*z* + 1/2; (iii) −*x* + 1, −*y* + 2, −*z* + 1; (iv) *x*, *y* − 1, *z*; (v) −*x*, −*y* + 1, −*z* + 1; (vi) −*x*, *y* − 1/2, −*z* + 1/2.

Fig. 1

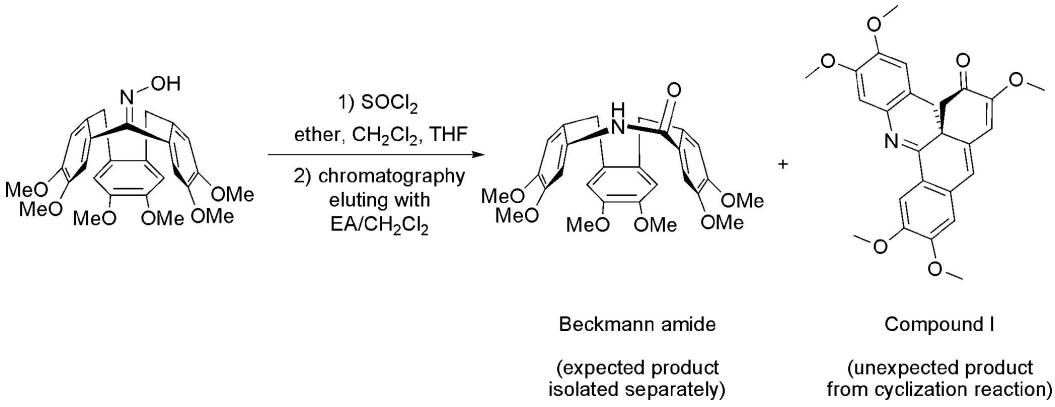
N
OH
MeO
MeO
MeO
OMe
OMe
OMe
1) SOCl2
ether, CH2Cl2, THF
2) chromatography
eluting with
EA/CH2Cl2
H
N
O
MeO
MeO
MeO
OMe
OMe
OMe
+
O
O
O
O
N
O
O
Beckmann amide
(expected product
isolated separately)
Compound I
(unexpected product
from cyclization reaction)

Fig. 2

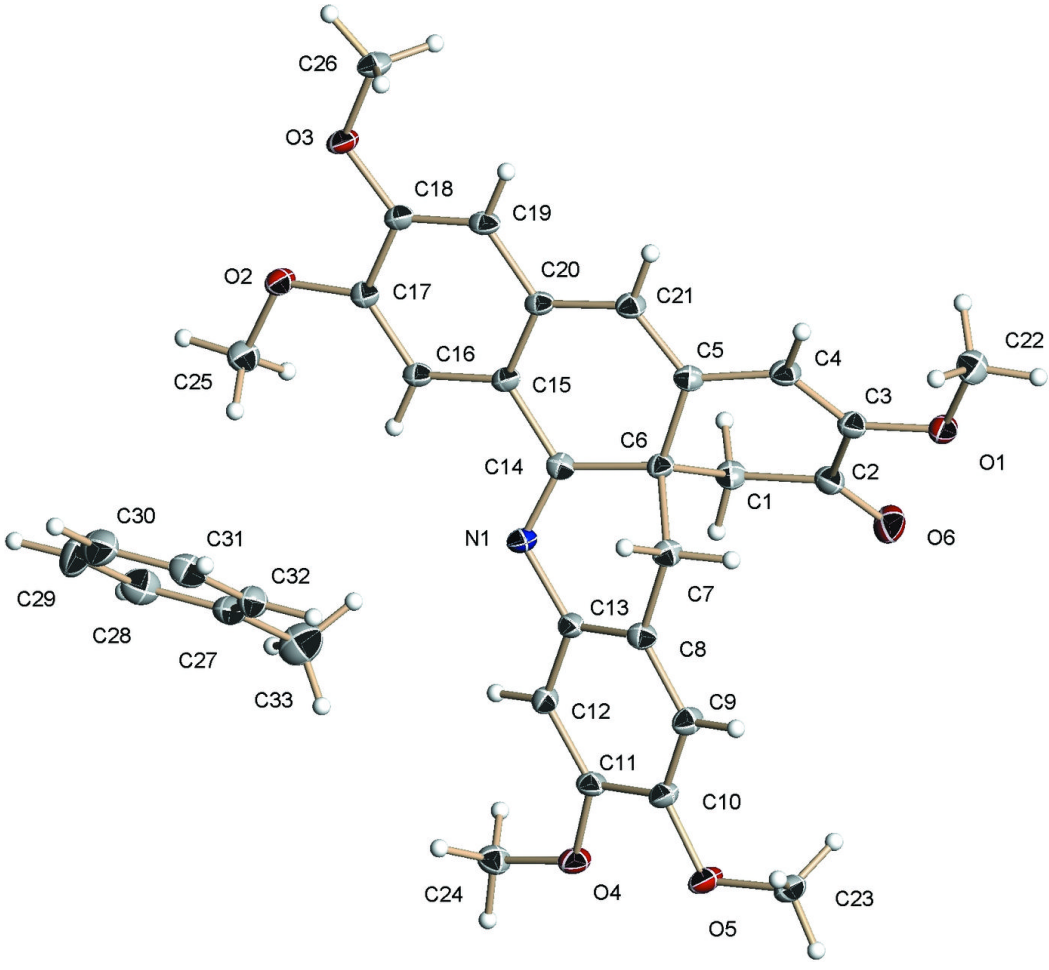
C26
O3
C18
C19
O2
C17
C20
C21
C22
C25
C16
C15
C5
C4
C3
O1
C6
C14
C2
C1
O6
C30
C31
N1
C32
C29
C7
C13
C28
C27
C8
C33
C12
C9
C11
C10
C24
O4
C23
O5

Fig. 3