Monoclinic
$P2_1$
$a = 10.8176\,(18)$ Å
$b = 9.7701\,(13)$ Å
$c = 15.242\,(3)$ Å
$\beta = 108.832\,(18)°$
$V = 1524.6\,(4)$ Å^3
$Z = 2$
$D_x = 1.243$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 12.6–20.1°$
$\mu = 1.326$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
$0.65 \times 0.32 \times 0.20$ mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$2\theta/\omega$ scans
Absorption correction: numerical (Coppens *et al.*, 1965)
$T_{\min} = 0.48$, $T_{\max} = 0.78$
7255 measured reflections
3707 independent reflections (plus 3294 Friedel-related reflections)

5804 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 27.49°$
$h = -14 \rightarrow 13$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 19$
3 standard reflections every 100 reflections intensity decay: 13.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.105$
$S = 1.033$
7001 reflections
366 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.062P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.008$

$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.64$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = $-0.008\,(9)$

Table 1. *Selected geometric parameters (Å, °)*

Se1—N1	1.791 (3)	S1—N1	1.607 (3)
Se1—C21	1.932 (4)	S1—C31	1.769 (4)
Se1—C11	1.985 (3)		
N1—Se1—C21	96.63 (16)	C12—C11—C16	122.6 (3)
N1—Se1—C11	116.66 (14)	C12—C11—Se1	110.6 (2)
C21—Se1—C11	96.95 (15)	C16—C11—Se1	124.6 (2)
S1—N1—Se1	112.55 (17)		

The data collection covered a hemisphere of reciprocal space to include the Bijvoet pairs. The average intensity of the standard reflections decayed by 13.2%, and the colour of the specimen changed from colourless to red after the intensity measurement. Measured intensities were corrected by polynomial fitting of the variation of standards, although the chemical reason for this phenomenon was not clear. All H atoms were placed in geometrically calculated positions and refined using a riding model because of the large thermal displacement of the *tert*-butyl groups. Although C121, C123 and C143 had large anisotropic parameters, no disorder treatment could be applied. The final Flack parameter (Flack, 1983) was $-0.008\,(9)$, while the refinement of the inverted structure gave a value of 1.01 (2).

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1990). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1092). Services for accessing these data are described at the back of the journal.

References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Furmanova, N. G., Gerr, R. G., Krasnov, V. P. & Naddaka, V. I. (1984). *Zh. Strukt. Khim.* **25**, 166–169.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kálmán, A., Duffin, B. & Kucsman, Á. (1971). *Acta Cryst.* B**27**, 586–594.

Molecular Structure Corporation (1992). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Rigaku Corporation (1990). *Rigaku/AFC Diffractometer Control Software*. Rigaku Corporation, Akishima, Tokyo, Japan.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Taka, H., Shimizu, H., Iwasaki, F., Yasui, M. & Kamigata, N. (1999). *J. Org. Chem.* In the press.

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Tetracyclohexyloxaquaterene[†]

Robert Pajewski,[a] Agnieszka Pęcak,[a] Ryszard Ostaszewski[a] and Janusz Jurczak[a,b]

[a]*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland, and* [b]*Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland. E-mail: apecak@ichf.edu.pl*

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Abstract

The title compound, $C_{40}H_{48}O_4$, has twofold crystallographic symmetry and exhibits a square-like conformation, with furan rings positioned alternately up–down–up–down, nearly orthogonal to the mean plane of the macrocyclic ring. This is the most orthogonal position of the furan rings towards the mean plane of the macrocyclic ring among known compounds of this type.

[†] Systematic name: 21,22,23,24-tetraoxapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{13,16}]tetracosa-3,5,8,10,13,15,18,20-octaene-2,7,12,17-tetraspirocyclohexane.

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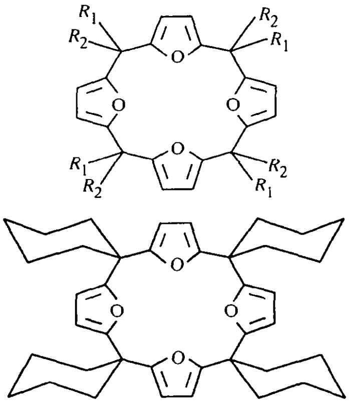
Comment

The capability to self-assemble is a property of some furan-based compounds. Macrocyclic rings can be easily synthesized by acid-promoted condensation of furan and selected aldehydes and ketones. Tetraoxaquaterenes are also interesting due to their structural similarity to porphyrinogenes. The parent compounds with R_1/R_2 = H (two polymorphs; Hass *et al.*, 1988) and R_1/R_2 = Me (Hazell, 1989), and a silver complex of the compound with R_1/R_2 = Et (Kretz *et al.*, 1994) are known. Also, the dicationic form of the derivative with R_1/R_2 = H, as the diperchlorate, was characterized by X-ray crystallography (Vogel *et al.*, 1988).

The fully symmetric title molecule, (I), in solution shows C_2 symmetry in the crystal. The C_2 axis parallel to the crystal b axis passes through the centre of the macrocyclic ring.



(I)

The conformation of the molecule is square-like, with the furan rings adopting near orthogonal up–down–up–down geometry (Fig. 1). This is similar to that found in the compounds with R_1/R_2 = H (monoclinic form) and R_1/R_2 = Me, and the nitrogen analogue. The angle between the mean planes of neighbouring furan rings is 88.9 (1)°. The conformation of the macrocyclic ring in the present case is closer to square symmetry than predicted by the MNDO method (the predicted dihedral angle between neighbouring furan rings is 66.6°; Cuthbertson & Glidewell, 1983). The furan rings are tilted only slightly away from the cavity so that the dihedral angles between the mean planes of opposite-lying rings are 4.5 (1) and 5.2 (1)°. The angles between the mean plane of the macrocyclic ring and the furan-ring planes are 92.1 (1) and 87.7 (1)°. This is the most orthogonal position found among this class of compounds, *cf.* R_1/R_2 = Me 77–80°, R_1/R_2 = H (monoclinic form) 76–80° and R_1/R_2 = H (triclinic form) *ca* 30°. In all the compounds examined previously, the furan O atoms were directed slightly towards the inside of the cavity. This tendency could thus be attributed to the bulky cyclohexyl substituent interacting with the H atoms of the furan ring.

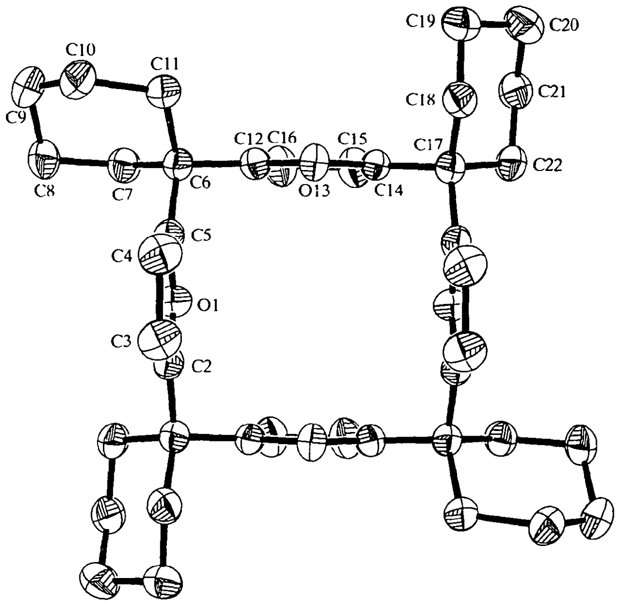


Fig. 1. *ORTEP*II (Johnson, 1976) plot of (I) with atom labels and 50% probability displacement ellipsoids for non-H atoms. H atoms have been omitted for clarity.

Inspection of the appropriate bond lengths and angles in the crystallographically unique part of the molecule shows that they are typical. The C3—C4 bond length is greater than that of C2—C3, which is a characteristic feature of non-annulene forms of such compounds; the same is observed for the thiophene (Vogel *et al.*, 1989) and pyrrole derivatives (Dolphin, 1978).

The packing in (I) (Fig. 2) is significantly different from that of the R_1/R_2 = Me analogue. In the present case, molecules are arranged in stacks with intramolecular voids positioned exactly over one another, while in the R_1/R_2 = Me compound, the methyl groups are positioned over the centre of the void.

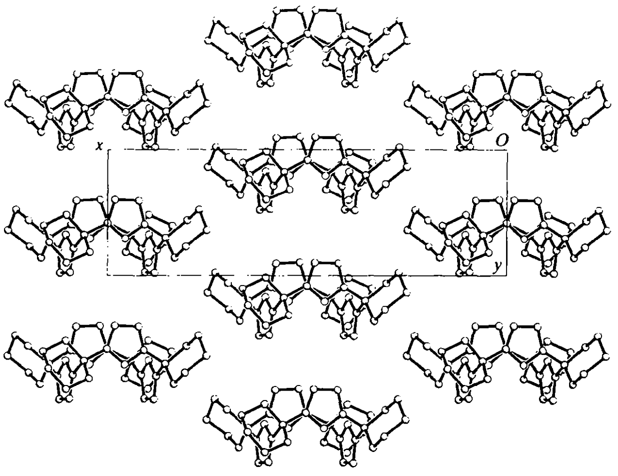


Fig. 2. The packing of (I) viewed down the *c* axis.

Cafeo *et al.* (1999) observed intra- and intermolecular C—H···π interactions among related structures. We have also found a short intermolecular distance which could be considered a C—H···π interaction [H21*A*···π 2.88 Å and C21—H21*A*···π 156°; π = O1···C5($x-\frac{1}{2}$, $y-\frac{1}{2}$, z)].

Experimental

Compound (I) was prepared using an improvement of the procedure of Brown & Hutchinson (1978). Precooled sulfuric acid (5 ml, 90.5%) was added dropwise to a precooled (273–278 K) stirred mixture of cyclohexanone (20 mmol), furan (1.44 ml, 20 mmol) and dioxane (30 ml). Upon addition of sulfuric acid, the reaction mixture turned red and some precipitation of product was observed. The reaction mixture was stirred overnight at room temperature, then water (50 ml) was added and the acid was neutralized with an aqueous sodium hydroxide solution (20%). The crude product was filtered off, washed with water (2 × 10 ml), methanol (2 × 10 ml) and recrystallized from toluene to give the title compound as colourless prisms (45% yield).

Crystal data

$C_{40}H_{48}O_4$
M_r = 592.78
Monoclinic
$C2/c$
a = 21.897 (2) Å
b = 6.8919 (5) Å
c = 21.694 (2) Å
β = 90.953 (7)°
V = 3273.4 (5) Å^3
Z = 4
D_x = 1.203 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 22.32–45.37°
μ = 0.592 mm^{-1}
T = 293 (2) K
Prism
0.39 × 0.32 × 0.18 mm
Colourless

Data collection

Enraf–Nonius MACH3 diffractometer
ω–2θ scans
Absorption correction: none
3393 measured reflections
3303 independent reflections
2636 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.019
$\theta_{\rm max}$ = 74.07°
$h = 0 \rightarrow 27$
$k = 0 \rightarrow 8$
$l = -27 \rightarrow 27$
3 standard reflections
frequency: 50 min
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.051
$wR(F^2)$ = 0.135
S = 1.154
3303 reflections
199 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 2.0057P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.16 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.29 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C2	1.372 (2)	C12—C16	1.341 (2)
O1—C5	1.373 (2)	C12—O13	1.373 (2)
C2—C3	1.342 (2)	O13—C14	1.375 (2)
C2—C17^{i}	1.505 (2)	C14—C15	1.343 (2)
C3—C4	1.427 (3)	C14—C17	1.507 (2)
C4—C5	1.341 (2)	C15—C16	1.429 (2)
C5—C6	1.508 (2)	C17—C2^{i}	1.505 (2)
C6—C12	1.505 (2)		
C2—O1—C5	107.50 (14)	C16—C12—O13	109.43 (15)
C3—C2—O1	109.26 (15)	C16—C12—C6	134.53 (16)
C3—C2—C17^{i}	134.71 (17)	O13—C12—C6	116.02 (15)
O1—C2—C17^{i}	116.02 (15)	C12—O13—C14	107.34 (13)
C2—C3—C4	106.97 (17)	C15—C14—O13	109.26 (15)
C5—C4—C3	107.12 (17)	C15—C14—C17	135.15 (16)
C4—C5—O1	109.14 (15)	O13—C14—C17	115.56 (15)
C4—C5—C6	135.24 (16)	C14—C15—C16	107.01 (16)
O1—C5—C6	115.54 (15)	C12—C16—C15	106.97 (17)
C12—C6—C5	108.02 (13)	C2^{i}—C17—C14	108.04 (13)

Symmetry code: (i) $1-x, y, \frac{3}{2}-z$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *OpenMolEN* (Enraf–Nonius, 1997). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1288). Services for accessing these data are described at the back of the journal.

References

Brown, W. H. & Hutchinson, B. J. (1978). *Can. J. Chem.* **56**, 617–621.
Cafeo, G., Gianetto, M., Kohnke, F. H., La Torre, G. L., Parisi, M. F., Menzer, S., White, A. J. P. & Williams, D. J. (1999). *Chem. Eur. J.* **5**, 356–368.
Cuthbertson, A. F. & Glidewell, C. (1983). *J. Mol. Struct. Theochem.* **94**, 407–410.
Dolphin, D. (1978). *Porphyrins and Metalloporphyrins*, Vols. I–VII. New York: Academic Press.
Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1. Enraf–Nonius, Delft, The Netherlands.
Enraf–Nonius (1997). *OpenMolEN. Interactive Structure Solution Program*. Enraf–Nonius, Delft, The Netherlands.
Hass, W., Knipp, B., Sicken, M., Lex, J. & Vogel, E. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 409–410.
Hazell, A. (1989). *Acta Cryst.* C**45**, 137–140.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kretz, C. M., Gallo, E., Solari, E., Floriani, C., Chiesi-Villa, A. & Rizzoli, C. (1994). *J. Am. Chem. Soc.* **116**, 10775–10776.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Vogel, E., Hass, W., Knipp, B., Lex, J. & Schmickler, H. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 406–409.
Vogel, E., Röhring, P., Knipp, B., Herrmann, A., Pohl, M., Schmickler, H. & Lex, J. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1651–1655.