

Pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene-17,18-dione

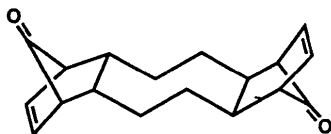
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Abstract. C₁₈H₂₀O₂, *M_r* = 268.4, monoclinic, *P*2₁/*n*, *a* = 6.4779 (4), *b* = 9.2310 (14), *c* = 12.0021 (12) Å, β = 98.392 (7)°, *V* = 710.0 (2) Å³, *Z* = 2, *D_x* = 1.255 g cm⁻³, λ(Cu *Kα*) = 1.54184 Å, μ = 5.95 cm⁻¹, *F*(000) = 288, *T* = 297 K, *R* = 0.034 for 1310 observations with *I* > 3σ(*I*) (of 1457 unique data). The molecule lies on a center of symmetry and the cyclooctane ring adopts the chair conformation. The near-zero torsion angle of the chair occurs at the ring-fusion bonds and has a magnitude of 0.8 (1)°. The C=C bond has a length of 1.325 (2) Å and the C=O bond length is 1.197 (2) Å. The C—C—C angle at the carbonyl bridge is small with a magnitude of 97.20 (9)°.

Experimental. The title compound was prepared by allowing *endo,endo,anti*-17,17,18,18-tetramethoxy-pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene (Garcia, Fronczek & McLaughlin, 1991*a*) to react with an 80% solution of glacial acetic acid in water at 328–332 K (Grimme & Wiechers, 1987). Crystals



of the title compound grown by slow cooling of toluene, m.p. 497–499 K, were suitable; a clear colorless crystal with dimensions 0.15 × 0.28 × 0.40 mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Cu *Kα* radiation and a graphite monochromator. Cell dimensions were determined from setting angles of 25 reflections having 30 > θ > 26°. The ω–2θ scans were designed for *I* = 25σ(*I*), subject to max. scan time = 90 s, scan rates varied from 0.61–3.30° min⁻¹. Two quadrants of data having 2 < θ < 75°, 0 ≤ *h* ≤ 8, –11 ≤ *k* ≤ 11, –15 ≤ *l* ≤ 15 were measured and corrected for background, Lorentz, polarization and absorption. Absorption corrections were based on ψ scans, with min. relative transmission coefficient 0.9097. Three standard reflections (400, 020, 004) were measured

every 10 000 s and exhibited only random intensity variation. 3228 measurements were made. The two equivalent quadrants were averaged, *R_{int}* = 0.013, yielding 1457 unique data of which 1310 had *I* > 3σ(*I*) and were used in the refinement. The structure was solved by direct methods using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refined by full-matrix least squares based upon *F*, with weights *w* = 4*F_o*²[σ²(*I*) + (0.02*F_o*²)]⁻¹, using the *Enraf–Nonius Structure Determination Package* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974), and anomalous coefficients of Cromer (1974). Heavy-atom coordinates were refined with anisotropic thermal parameters; H-atom coordinates were located by Δ*F* synthesis and were refined with isotropic thermal parameters. Final *R* = 0.034 for 1310 observed data (0.039 for all 1457 data), *wR* = 0.056 and *S* = 3.207 for 132 variables. Max. shift < 0.01σ in the final cycle, max. residual density 0.17, min. –0.12 e Å⁻³, and extinction coefficient *g* = 1.07 (8) × 10⁻⁵, where the factor (1 + *gI_c*)⁻¹ was applied to *F_c*. The fractional coordinates of the title compound are given in Table 1. Fig. 1 is a perspective drawing showing the atom numbering for the title molecule, and Fig. 2 shows the unit cell. Bond distances, angles, and selected torsion angles are presented in Table 2.†

Related literature. Single-bond distances which are analogous to C1–C6 and C4–C5 are found in 1,2,4,5,6,7,8,9-octachloro-10,10-dimethoxytricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one, 1.572 (3) and 1.573 (3) Å (Galesic, Matijasic & Bruvo, 1985); 3,4,5,6-tetrachloro-12,12-dimethoxy-9,10-bis(methoxycarbonyl)-*exo,endo*-pentacyclo[6.2.1.1^{3,6}.0^{2,7}]-dodeca-4,9-diene, 1.550 (4) and 1.556 (3) Å (Battiste, Griggs, Sackett, Coxon & Steel, 1987); [(9,10-η²:11σ)-3,4,5,6-tetrachloro-12,12-dimethoxy-9,10-bis(methoxycarbonyl)-*exo,endo*-tetracyclo[6.2.1.-

† Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54060 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Coordinates and equivalent isotropic thermal parameters

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
O	0.3844 (2)	0.5074 (1)	0.63879 (9)	6.66 (3)
C1	0.6532 (2)	0.3167 (1)	0.63494 (9)	4.33 (2)
C2	0.6898 (2)	0.2351 (1)	0.7444 (1)	5.08 (2)
C3	0.5066 (2)	0.1953 (1)	0.77108 (9)	4.91 (3)
C4	0.3378 (2)	0.2468 (1)	0.68085 (9)	4.19 (2)
C5	0.3536 (2)	0.1585 (1)	0.57075 (8)	3.28 (2)
C6	0.5705 (2)	0.2075 (1)	0.53867 (8)	3.33 (2)
C7	0.4455 (2)	0.3851 (1)	0.65012 (9)	4.57 (2)
C8	0.7295 (1)	0.0902 (1)	0.52349 (8)	3.57 (2)
C9	0.3173 (2)	-0.0031 (1)	0.58623 (9)	3.40 (2)

Table 2. Bond distances (Å), angles (°) and selected torsion angles (°)

O—C7	1.197 (2)	C4—C5	1.569 (2)
C1—C2	1.503 (2)	C4—C7	1.526 (2)
C1—C6	1.567 (1)	C5—C6	1.576 (1)
C1—C7	1.521 (2)	C5—C9	1.526 (1)
C2—C3	1.325 (2)	C6—C8	1.524 (1)
C3—C4	1.500 (2)	C8—C9'	1.535 (1)
C2—C1—C6	108.41 (9)	C6—C5—C9	117.97 (8)
C2—C1—C7	97.6 (1)	C1—C6—C5	103.03 (8)
C6—C1—C7	98.17 (8)	C1—C6—C8	112.38 (8)
C1—C2—C3	108.5 (1)	C5—C6—C8	117.87 (8)
C2—C3—C4	108.8 (1)	O—C7—C1	131.4 (1)
C3—C4—C5	108.26 (9)	O—C7—C4	131.4 (1)
C3—C4—C7	97.4 (1)	C1—C7—C4	97.20 (9)
C5—C4—C7	98.21 (9)	C6—C8—C9'	115.00 (7)
C4—C5—C6	103.09 (8)	C5—C9—C8'	115.00 (8)
C4—C5—C9	112.05 (8)		
C9—C5—C6—C8	0.8 (1)	C4—C5—C6—C1	0.5 (1)
C1—C2—C3—C4	0.4 (1)	C5—C6—C8—C9'	74.8 (1)
C6—C5—C9—C8'	-76.6 (1)	C6—C8—C9—C5'	-117.8 (1)

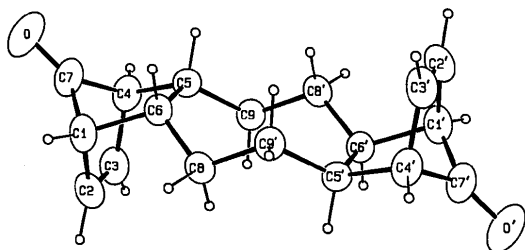
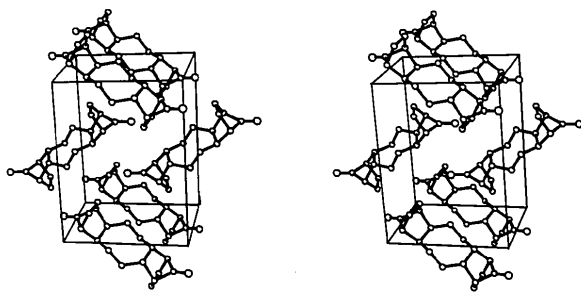


Fig. 1. ORTEP (Johnson, 1965) drawing of the title molecule. Heavy atoms represented as 40% probability ellipsoids and H atoms as circles of arbitrary radius.

Fig. 2. Stereoview of unit cell. *c* is vertical, *b* is horizontal and *a* is into the plane of the paper.

1^{3,6}.0^{2,7}]dodeca-4,9-dien-11-yl](η^5 -cyclopentadienyl)-nickel(II), 1.546 (3) and 1.550 (3) Å (Battiste *et al.*, 1987); 1,2,3,4,7,7-hexachloro-5,6-bis(chloromethyl)-bicyclo[2.2.1]hept-2-ene [Alodan (Hoechst)[®]], 1.568 (7) and 1.549 (7) Å (Kennard, Smith & Palm, 1981); *endo,endo,anti*-1,6,7,8,9,14,15,16-octachloro-17,17,18,18-tetramethoxypentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene, 1.561 (3) and 1.555 (4) Å (Garcia *et al.*, 1991a); *endo,endo,anti*-17,17,18,18-tetramethoxypentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene, 1.566 (1) and 1.564 (1) Å (Garcia *et al.*, 1991a); *endo,endo,anti*-1,6,7,8,9,14,15,16-octachloropentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene, 1.553 (4) and 1.560 (3) Å (Garcia, Fronczek & McLaughlin, 1991b) are similar to those in the title compound: 1.567 (1) and 1.569 (2) Å, respectively. The bond angle C1—C7—C4 [97.20 (9)°] of the title compound is similar to the analogous bond angles of 1,2,4,5,6,7,8,9-octachloro-10,10-dimethoxytricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one [91.6 (1)°] (Galesic *et al.*, 1985); 3,4,5,6-tetrachloro-12,12-dimethoxy-9,10-bis(methoxycarbonyl)-*exo,endo*-pentacyclo[6.2.1.-1^{3,6}.0^{2,7}]dodeca-4,9-diene and [(9,10- η^2 :11 σ)-3,4,5,6-tetrachloro-12,12-dimethoxy-9,10-bis(methoxycarbonyl)-*exo,endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-11-yl](η^5 -cyclopentadienyl)nickel(II) [90.9 (2) and 90.7 (2)°, respectively] (Battiste *et al.*, 1987); 1,2,3,4,7,7-hexachloro-5,6-bis(chloromethyl)-bicyclo[2.2.1]hept-2-ene [Alodan (Hoechst)[®]] [92.9 (4)°] (Kennard *et al.*, 1981); *endo,endo,anti*-1,6,7,8,9,14,15,16-octachloro-17,17,18,18-tetramethoxypentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene [90.9 (2)°] (Garcia *et al.*, 1991a); *endo,endo,anti*-17,17,18,18-tetramethoxypentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene [93.88 (8)°] (Garcia *et al.*, 1991a); *endo,endo,anti*-1,6,7,8,9,14,15,16-octachloropentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene [92.2 (2)°] (Garcia *et al.*, 1991b). The C7—O bond distance of 1.197 (2) Å is in accord with literature data (Coxon, O'Connell & Steel, 1985; Blom, Kanters & Kroon, 1981; Balasubrahmanyam, Usha & Venkatesan, 1981). The angle C1—C7—C4 at the carbonyl bridge is small with a magnitude of 97.20 (9)°.

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Structure of 2,3-Bis(2-pyridyl)pyrazine

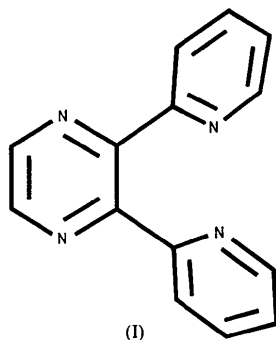
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Abstract. $C_{14}H_{10}N_4$ (dpp), $M_r = 234.26$, orthorhombic, $Pbcn$, $a = 16.439$ (3), $b = 9.448$ (2), $c = 7.478$ (2) Å, $V = 1161.5$ (3) Å³, $Z = 4$, $D_x = 1.34$ g cm⁻³, graphite-monochromated Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.8$ cm⁻¹, $F(000) = 488$, $T = 294$ (1) K, $R = 0.048$ for 630 observed reflections. The molecule has crystallographic twofold rotational symmetry. The rotation axis passes through the mid-points of the pyrazine carbon—carbon bonds. The pyrazine and pyridine rings are planar, with mean deviations from planarity of 0.007 and 0.001 Å, respectively; the dihedral angle between pyrazine and pyridine rings is 42.2° and between the two pyridine rings is 54.1°.

Experimental. Colorless, parallelepiped crystal, dimensions 0.32 × 0.37 × 0.43 mm. The compound (I) was crystallized from an aqueous manganese(II) perchlorate solution. Nicolet R3m/V diffractometer,



(I)

$\omega/2\theta$ scans of 2–15° min⁻¹, $2\theta_{\max} = 45^\circ$, $h = 0$ to 18, $k = -11$ to 0, $l = 0$ to 9, 756 unique measurements, 630 observed [$I > 3\sigma(I)$]. Unit-cell dimensions determined by least-squares fit to settings for 47 reflections ($27 < 2\theta < 45^\circ$). No absorption correction; three standards monitored (332, 522, 114; $\pm 1\%$), 9.0 h of X-ray exposure. Solved by direct methods; full-matrix least-squares refinement on F , $R = 0.0478$, $wR = 0.0694$, $S = 2.49$, $(\Delta/\sigma)_{\max} = 0.01$, 102 variables including positional and anisotropic thermal parameters for the non-H atoms. H atoms were located by difference Fourier techniques and refined isotropically. Function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$; $\sigma(F_o)$ was estimated from counting statistics. Final difference Fourier peaks ranged from -0.19 to 0.21 e Å⁻³. Computer programs from *SHELXTL* (Sheldrick, 1986), scattering factors (Cromer & Waber, 1974) and real and imaginary anomalous-dispersion corrections (Cromer, 1974). Final atomic coordinates are given in Table 1,* and distances and angles in Table 2; the molecule is shown in Fig. 1.

Related literature. A related compound, 2,3-bis(2-pyridyl)quinoxaline (dpq), has been structurally characterized (Rasmussen, Richter, Yi, Place &

* Lists of structure factors, anisotropic thermal parameters, a summary of crystallographic details and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54046 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.