Related literature. The structures of dimethylfulvene at 248 K (Norman & Post, 1961), and 5-(2,4-cyclopentadien-1-ylidene)cyclooctanone (Cronan, Fronczek & McLaughlin, 1989) exhibit the expected single–double bond alternation within the fulvene ring system, as does the title compound. The bond angles C2—C1—C8 116·7 (2) and C4—C5—C6 116·6 (2)° of the title compound are similar to the analogous bond angles of dimethylfulvene, 114·0 (6)°, and 5-(2,4-cyclopentadien-1-ylidene)cyclooctanone, 116·6 (2)°.

The eight-membered ring of the title molecule adopts a chair–boat conformation with bond distances and angles similar to those found for 1,5-cyclooctadione (Miller & McPhail, 1979) and 5-(2,4-cyclopentadien-1-ylidene)cyclooctanone (Cronan, Fronczek & McLaughlin, 1989). The close intermolecular contact between the 1 and 5 positions of the eight-membered ring of 1,5-cyclooctadione, 2·963 (8) Å, 5-(2,4-cyclopentadien-1-ylidene)cyclooctanone, 3·018 (2) Å, and the title compound, 2·957 (2) Å, are similar.

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References

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

CRONAN, J. M. JR, FRONCZEK, F. R. & MCLAUGHLIN, M. L. (1989). *Acta Cryst.* C**45**, 1063–1065.

FRENZ, B. A. & OKAYA, Y. (1980). *Enraf–Nonius Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

MILLER, R. W. & MCPHAIL, A. T. (1979). *J. Chem. Soc. Perkin Trans.* 2, pp. 1527–1531.

NORMAN, N. & POST, B. (1961). *Acta Cryst.* **14**, 503–507.

STONE, K. J. & LITTLE, R. D. (1985). *J. Org. Chem.* **49**, 1849–1853.

Acta Cryst. (1990). C**46**, 924–926

7,8-Dihydro-1,6,11-trimethoxy-5,12-naphthacenedione

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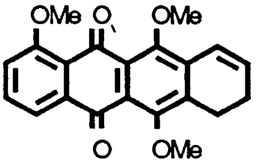
Abstract. $C_{21}H_{18}O_5$, $M_r = 350·4$, monoclinic, $P2_1/n$, $a = 12·853$ (3), $b = 8·183$ (2), $c = 17·506$ (4) Å, $\beta = 109·45$ (2)°, $V = 1736·1$ (7) Å^3, $Z = 4$, $D_x = 1·34$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·89$ cm^{-1}, $F(000) = 736$, $T = 295$ K. Final $R = 0·052$ for 1863 observed reflections. The average bond distances are C═O = 1·216 (4), O—C_{benz} = 1·367 (4), O—CH_3 = 1·426 (5), C—C_{benz} = 1·397 (5), C—C = 1·489 (5) Å and C═C = 1·346 (5) Å. The X-ray structure confirms the structure of one of the regioisomers formed in the reaction of aryne generated from 2-bromo-5,6-dihydro-1,4-dimethoxynaphthalene and 7-methoxycyanophthalide.



(1)

Experimental. The title compound (1) was prepared along with the other regioisomer, 9,10-dihydro-1,6,11-trimethoxy-5,12-naphthacenedione, by a reaction of 7-methoxy-1-oxo-1,3-dihydro-3-isobenzofurancarbonitrile and 2-bromo-1,5-dimethoxy-5,6-dihydronaphthalene in the presence of lithium diisopropylamide (LDA) and THF (Khanapure & Biehl, 1987). Two regioisomers were readily separated by flash chromatography. Crystals of (1) are pale-yellow plates, unit-cell parameters by least-squares fit of 25 reflections in the range $10 < 2\theta < 25°$, crystal dimensions 0·30 × 0·40 × 0·10 mm, space group $P2_1/n$ from systematic absences ($0k0$, k odd; $h0l$, $h + l$ odd); automatic Nicolet $R3m/V$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan mode (scan rate 3·0–15·0° min^{-1}, depending on intensity), 4436 measured reflections, 4015 independent reflections in the range $3 < 2\theta < 55°$,

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$R_{\text{int}} = 0{\cdot}015$, *hkl* range $h - 16 \rightarrow 15$, $k\ 0 \rightarrow 10$, $l\ 0 \rightarrow 22$, 1863 observed reflections with $I > 3{\cdot}0\sigma(I)$, $\sigma(I)$ from counting statistics; three standard reflections remeasured after every 100 reflections did not show any significant change in intensity (1·0%) during data collection; Lorentz–polarization correction, no absorption or extinction corrections. Structure solved by direct methods using *SHELXTL-Plus* (Sheldrick, 1988) and subsequent difference Fourier methods. Olefinic H atoms were located on difference Fourier maps and CH_2 and CH_3 H-atom positions were calculated. H atoms were included in the final refinement with fixed isotropic temperature factors (0·08 Å^2), fixed positional parameters for olefinic H atoms and geometric constraints (C—H = 0·96 Å) for CH_2, CH_3 and phenyl H atoms. Final full-matrix least-squares refinement (*SHELXTL-Plus*) converged to $R = 0{\cdot}052$, $wR = 0{\cdot}065$, $S = 1{\cdot}61$ for 235 parameters; $w = 1/[\sigma^2(F_o) + 0{\cdot}00065(F_o)^2]$, $\sum w(|F_o| - |F_c|)^2$ minimized; $(\Delta/\sigma)_{\max} = 0{\cdot}001$, $\Delta\rho_{(\max,\min)} = 0{\cdot}25$, $-0{\cdot}26\ \text{e}\ \text{Å}^{-3}$ in final difference Fourier map. Atomic scattering factors for C, H, and O were those stored in *SHELXTL-Plus* which were taken from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are given in Table 1,* bond lengths, angles and selected torsion angles are given in Table 2. The identification of the atoms and the configuration are shown in the thermal ellipsoid drawing (*SHELXTL-Plus*) of Fig. 1.

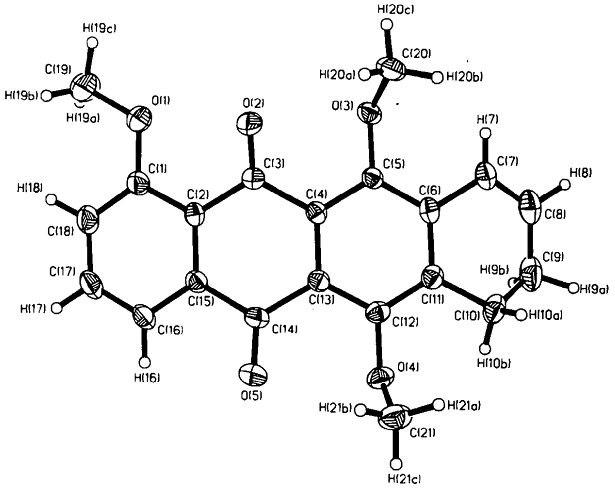

Fig. 1. Thermal-ellipsoid drawing (*SHELXTL-Plus*) of the molecule. Ellipsoids scaled to enclose 30% probability. H atoms are represented as spheres of arbitrary radii.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement coefficients* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*
O(1)	2740 (2)	− 1630 (4)	6103 (2)	66 (1)
O(2)	4298 (2)	659 (3)	6247 (1)	50 (1)
O(3)	6345 (2)	42 (3)	6095 (1)	44 (1)
O(4)	7872 (2)	387 (3)	9444 (1)	51 (1)
O(5)	5682 (2)	446 (4)	9318 (2)	73 (1)
C(1)	3074 (3)	− 1654 (4)	6920 (2)	47 (1)
C(2)	4088 (3)	− 878 (4)	7332 (2)	37 (1)
C(3)	4737 (3)	16 (4)	6903 (2)	34 (1)
C(4)	5948 (3)	167 (4)	7342 (2)	34 (1)
C(5)	6701 (3)	268 (4)	6921 (2)	36 (1)
C(6)	7831 (3)	410 (4)	7343 (2)	41 (1)
C(7)	8647 (3)	402 (5)	6909 (2)	54 (2)
C(8)	9715 (3)	92 (5)	7324 (3)	71 (2)
C(9)	10144 (3)	− 32 (6)	8203 (3)	77 (2)
C(10)	9434 (3)	747 (5)	8623 (2)	54 (2)
C(11)	8217 (3)	526 (4)	8191 (2)	41 (1)
C(12)	7469 (3)	429 (4)	8610 (2)	40 (1)
C(13)	6337 (3)	215 (4)	8197 (2)	36 (1)
C(14)	5525 (3)	− 19 (4)	8630 (2)	43 (1)
C(15)	4472 (3)	− 880 (4)	8176 (2)	39 (1)
C(16)	3879 (3)	− 1625 (5)	8620 (2)	49 (1)
C(17)	2911 (3)	− 2411 (5)	8204 (3)	60 (2)
C(18)	2507 (3)	− 2431 (5)	7367 (2)	57 (2)
C(19)	1749 (3)	− 2432 (7)	5663 (3)	103 (3)
C(20)	6189 (3)	1494 (5)	5609 (2)	58 (2)
C(21)	7930 (4)	1937 (5)	9835 (2)	68 (2)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å), *bond angles and torsion angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(1)	1·349 (4)	O(1)—C(19)	1·412 (5)
O(2)—C(3)	1·218 (4)	O(3)—C(5)	1·377 (4)
O(3)—C(20)	1·435 (4)	O(4)—C(12)	1·376 (4)
O(4)—C(21)	1·432 (5)	O(5)—C(14)	1·214 (4)
C(1)—C(2)	1·413 (4)	C(1)—C(18)	1·388 (6)
C(2)—C(3)	1·488 (5)	C(2)—C(15)	1·394 (4)
C(3)—C(4)	1·494 (4)	C(4)—C(5)	1·400 (5)
C(4)—C(13)	1·412 (4)	C(5)—C(6)	1·398 (4)
C(6)—C(7)	1·487 (6)	C(6)—C(11)	1·403 (5)
C(7)—C(8)	1·346 (5)	C(8)—C(9)	1·456 (7)
C(9)—C(10)	1·492 (7)	C(10)—C(11)	1·504 (4)
C(11)—C(12)	1·393 (6)	C(12)—C(13)	1·403 (4)
C(13)—C(14)	1·493 (6)	C(14)—C(15)	1·497 (4)
C(15)—C(16)	1·396 (6)	C(16)—C(17)	1·375 (5)
C(17)—C(18)	1·383 (6)		

C(1)—O(1)—C(19)	118·9 (3)	C(5)—O(3)—C(20)	116·3 (2)
C(12)—O(4)—C(21)	115·3 (3)	O(1)—C(1)—C(2)	116·7 (3)
O(1)—C(1)—C(18)	124·2 (3)	C(2)—C(1)—C(18)	119·1 (3)
C(1)—C(2)—C(3)	122·7 (3)	C(1)—C(2)—C(15)	118·8 (3)
C(3)—C(2)—C(15)	118·4 (3)	O(2)—C(3)—C(2)	121·8 (3)
O(2)—C(3)—C(4)	121·7 (4)	C(2)—C(3)—C(4)	116·4 (3)
C(3)—C(4)—C(5)	121·2 (3)	C(3)—C(4)—C(13)	119·3 (3)
C(5)—C(4)—C(13)	119·5 (3)	O(3)—C(5)—C(4)	119·9 (3)
O(3)—C(5)—C(6)	119·3 (3)	C(4)—C(5)—C(6)	120·3 (3)
C(5)—C(6)—C(7)	121·0 (3)	C(5)—C(6)—C(11)	120·3 (4)
C(7)—C(6)—C(11)	118·7 (3)	C(6)—C(7)—C(8)	119·4 (4)
C(7)—C(8)—C(9)	122·9 (5)	C(8)—C(9)—C(10)	114·4 (3)
C(9)—C(10)—C(11)	113·9 (3)	C(6)—C(11)—C(10)	118·8 (4)
C(6)—C(11)—C(12)	119·4 (3)	C(10)—C(11)—C(12)	121·8 (3)
O(4)—C(12)—C(11)	118·5 (3)	O(4)—C(12)—C(13)	120·3 (3)
C(11)—C(12)—C(13)	121·0 (3)	C(4)—C(13)—C(12)	119·4 (3)
C(4)—C(13)—C(14)	118·3 (3)	C(12)—C(13)—C(14)	122·3 (3)
O(5)—C(14)—C(13)	123·4 (3)	O(5)—C(14)—C(15)	119·7 (4)
C(13)—C(14)—C(15)	116·9 (3)	C(2)—C(15)—C(14)	120·0 (3)
C(2)—C(15)—C(16)	121·6 (3)	C(14)—C(15)—C(16)	118·3 (3)
C(15)—C(16)—C(17)	118·4 (3)	C(16)—C(17)—C(18)	121·4 (4)
C(1)—C(18)—C(17)	120·7 (3)		

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* Anisotropic temperature factors, bond lengths, bond angles, torsion angles, H-atom parameters and lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52442 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Related literature. The synthesis of anthracycline antibiotics (Arcamone, 1981) is of great interest since they are important anticancer drugs. The 1,4-dipolar-aryne reaction is very useful for the preparation of tetracyclic intermediates (Khanapure & Biehl, 1990) in the synthesis of anthracyclinones (Krohn, 1986). One of the important factors involved in this strategy is the control of regiochemistry in the aryne reaction. The title compound is one of the intermediates involved in the anthracyclinone synthesis.

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References

Arcamone, F. (1981). *Doxorubicin Anticancer Antibiotics.* New York: Academic Press.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press (Present distributor Kluwer Academic Publishers, Dordrecht.)

Khanapure, S. P. & Biehl, E. R. (1987). *Abstracts of Papers.* 194th National Meeting of the American Chemical Society, Washington; ORGN 48.

Khanapure, S. P. & Biehl, E. R. (1990). *J. Org. Chem.* Submitted.

Krohn, K. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, 790–807.

Sheldrick, G. M. (1988). *SHELXTL-Plus. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Nicolet Instrument Corporation, Madison, Wisconsin, USA.

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Structure of a Pentacyclic Cage Enone

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Abstract. 8-Methylene-1-phenylpentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-11-one (2*a*), $C_{18}H_{16}O$, $M_r = 248{\cdot}35$, monoclinic, $P2_1/n$, $a = 10{\cdot}359$ (2), $b = 6{\cdot}579$ (1), $c = 19{\cdot}553$ (3) Å, $\beta = 102{\cdot}78$ (1)°, $V = 1299{\cdot}9$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}270$ g cm,$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71973$ Å, $\mu = 0{\cdot}80$ cm^{-1}, $F(000) = 528$, $T = 295$ K, $R = 0{\cdot}0587$ for 1967 reflections. Compound (2*a*) is a strained open-ended cage compound composed of four fused five-membered rings in envelope conformations and a planar four-membered ring. The molecule contains an exocyclic methylene and a ketone moiety. The two cross bonds in a 1–3 relationship to the methylene and ketone π systems are elongated to 1·587 (7) and 1·595 (3) Å which is consistent with a postulated through bond coupling in similar molecules. The ketone and methylene systems with attached atoms are each planar with an interplanar angle of 65·0 (2)°.

Experimental. As part of a program that is concerned with the synthesis and chemistry of novel polycyclic cage compounds (Marchand, 1989), the Wittig reaction of 1-phenylpentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (1) (Marchand, Annapurna, Reddy, Watson & Nagl, 1989) with $Ph_3P{=}CH_2$ has been studied (see scheme 1). This reaction potentially can afford the two cage enones (2*a*) and (2*b*); however, only (2*a*) was isolated (48% yield). A colorless crystal of dimensions $0{\cdot}65 \times 0{\cdot}20 \times 0{\cdot}15$ mm was mounted on a Nicolet $R3m/\mu$ update of a $P2_1$ diffractometer; data collected in the ω mode ($3 \leq 2\theta \leq 55°$) using a variable scan rate (4–29·3° min^{-1}); graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($22{\cdot}38 \leq 2\theta \leq 27{\cdot}63°$), angles measured by a centering routine, systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) consistent with space group $P2_1/n$; monitored reflections $\bar{3}21$ and $22\bar{3}$ showed variations of less than ±2%; 3405 reflections collected ($-13 \leq h \leq 13$, $0 \leq k \leq 8$, $0 \leq l \leq 25$), 2988 unique ($R_{\text{int}} = 0{\cdot}009$), equivalent reflections averaged, 1967 with $I \geq 3\sigma(I)$; Lorentz–polarization corrections applied, ψ-scan empirical absorption correction (transmission factors 0·960–0·921); structure solved by direct methods, block-cascade least-squares refinement, H atoms located in difference map and refined with isotropic thermal parameters; final $R = 0{\cdot}0587$, $wR = 0{\cdot}0520$ ($R = 0{\cdot}0908$ and $wR = 0{\cdot}0550$

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