C6	0.2184 (4)	0.0187 (3)	0.1934 (1)	0.0689 (8)
Cl7	0.0849 (8)	0.1731 (6)	0.1051 (3)	0.0673 (2)
Cl8	−0.2972 (9)	−0.2119 (6)	0.2151 (3)	0.0715 (3)
C9	−0.2484 (3)	−0.0057 (2)	0.1131 (9)	0.0478 (6)
C10	−0.3437 (3)	0.1236 (2)	0.1263 (1)	0.0534 (7)
O11	−0.3501 (2)	0.1634 (2)	0.1791 (8)	0.0684 (5)
N12	−0.4243 (3)	0.1808 (2)	0.0780 (1)	0.0665 (7)
N13	−0.2015 (3)	−0.0189 (2)	0.0471 (8)	0.0555 (6)
C14	−0.1889 (3)	−0.1343 (2)	0.0169 (1)	0.0487 (7)
C15	−0.1921 (3)	−0.2505 (2)	0.0493 (1)	0.0521 (7)
C16	−0.1843 (3)	−0.3691 (2)	0.0203 (1)	0.0525 (7)
C17	−0.1771 (4)	−0.3717 (3)	−0.0450 (1)	0.0616 (8)
C18	−0.1729 (3)	−0.2593 (3)	−0.0781 (1)	0.0590 (7)
C19	−0.1761 (3)	−0.1374 (2)	−0.0486 (1)	0.0499 (6)
C20	−0.1673 (4)	−0.0211 (3)	−0.0858 (1)	0.0609 (8)
C21	−0.1723 (7)	−0.0287 (4)	−0.1565 (1)	0.109 (1)
O22	−0.1507 (3)	0.0856 (2)	−0.0621 (8)	0.068 (6)
C23	−0.1770 (4)	−0.4905 (3)	0.0564 (1)	0.072 (9)

Table 2. *Geometric parameters* (Å, °)

C1—C2	1.406 (3)	C10—N12	1.336 (3)
C1—C6	1.387 (3)	N13—C14	1.367 (2)
C1—Cl7	1.731 (2)	C14—C15	1.395 (3)
C2—C3	1.391 (3)	C14—C19	1.412 (3)
C2—C9	1.510 (3)	C15—C16	1.383 (3)
C3—C4	1.398 (3)	C16—C17	1.405 (3)
C3—Cl8	1.748 (2)	C16—C23	1.481 (3)
C4—C5	1.347 (4)	C17—C18	1.368 (3)
C5—C6	1.404 (4)	C18—C19	1.417 (3)
C9—C10	1.541 (3)	C19—C20	1.452 (3)
C9—N13	1.468 (2)	C20—C21	1.521 (3)
C10—O11	1.209 (3)	C20—O22	1.227 (3)
C6—C1—Cl7	117.6 (2)	O11—C10—N12	124.2 (2)
C2—C1—Cl7	119.1 (2)	C9—N13—C14	123.9 (2)
C2—C1—C6	123.3 (2)	N13—C14—C19	119.9 (2)
C1—C2—C9	122.7 (2)	N13—C14—C15	121.4 (2)
C1—C2—C3	115.1 (2)	C15—C14—C19	118.7 (2)
C3—C2—C9	122.2 (2)	C14—C15—C16	123.0 (2)
C2—C3—Cl8	120.3 (2)	C15—C16—C23	121.6 (2)
C2—C3—C4	123.0 (2)	C15—C16—C17	118.0 (2)
C4—C3—Cl8	116.7 (2)	C17—C16—C23	120.4 (2)
C3—C4—C5	119.2 (2)	C16—C17—C18	120.3 (2)
C4—C5—C6	121.3 (3)	C17—C18—C19	122.0 (2)
C1—C6—C5	117.9 (2)	C14—C19—C18	117.9 (2)
C2—C9—N13	114.8 (2)	C18—C19—C20	119.8 (2)
C2—C9—C10	111.4 (2)	C14—C19—C20	122.3 (2)
C10—C9—N13	111.5 (2)	C19—C20—O22	121.8 (2)
C9—C10—N12	116.4 (2)	C19—C20—C21	120.4 (3)
C9—C10—O11	119.2 (2)	C21—C20—O22	117.8 (3)

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71330 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1041]

References

Beurskens, G., Noordik, J. H. & Beurskens, P. T. (1980). *Cryst. Struct. Commun.* **9**, 23–28.

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, Univ. of Nijmegen, The Netherlands.

Domenicano, A. & Murray-Rust, P. (1979). *Tetrahedron Lett.* **24**, 2283–2286.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Pauwels, R., Andries, K., Debyser, Z., Van Daele, P., Schols, D., Stoffels, P., De Vreese, K., Woestenborghs, R., Vandamme, A., Janssen, C. G. M., Anne, J., Cauwenbergh, G., Desmyter, J., Heykants, J., Janssen, M. A. C., De Clercq, E. & Janssen, P. A. J. (1993). *Proc. Natl Acad. Sci. USA*, **90**, 1711–1715.

Siemens (1989*a*). *P3/PC Diffractometer Program.* Version 3.13. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1989*b*). *XDISK. Data Reduction Program.* Version 3.11. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1989*c*). *XEMP. Empirical Absorption Correction Program.* Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1993). C**49**, 1963–1965

Structure of *syn*-7,8-Benzo-9,10-(9′,10′-phenanthro)tricyclo[4.2.2.$2^{2,5}$]dodeca-3,7,9-triene†

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Abstract

The double bond in the title compound, produced as a single stereoisomer in the $4\pi_s + 4\pi_s$ photocycloaddition of dibenz[*a*,*c*]anthracene with 1,3-cyclohexadiene, is established to be *syn* to the phenanthrene moiety, as predicted by the principle of maximum secondary orbital overlap. Two long interannular bonds, 1.610 (5) and 1.612 (5) Å, are present.

† Alternative name: 9,10,13,14-tetrahydro-9,14-*o*-benzeno-10,13-ethanocycloocta[1,2-*l*]phenanthrene.

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Comment

The title compound was prepared by the photo-addition of dibenz[*a*,*c*]anthracene with 1,3-cyclohexadiene in de-aerated benzene (Yang, Masnovi, Chiang, Wang, Shou & Yang, 1981). The cyclohexadiene-derived ring (C1*a*, C14*a*, C15*a*, C16*a*, C21*a* and C22*a*) of the title compound is in a boat configuration. The two independent sp^3–sp^3 (C15—C15*a*, C22—C22*a*) interannular single-bond distances are significantly longer [1.610 (5) and 1.612 (5) Å] than the usual value of about 1.54 Å. However, similarly long distances have been reported for the corresponding bonds of related structures (Ehrenberg, 1966, 1968; Dougherty, Hounshell, Schlegel, Bell & Mislow, 1976). Table 2 gives dihedral angles at the bridgehead positions, as well as a few selected torsion angles. No noteworthy intermolecular interactions are present. The double bond is located *syn* to the phenanthrene moiety, as predicted by consideration of secondary orbital interactions (Yang, Gau, Kim, Masnovi, Rafalko, Ezell & Lenz, 1990). Close intramolecular contacts (2.484 and 2.523 Å) involve the two *endo* H atoms on the cyclohexadiene-derived ring (H16*b* and H21*b*) with the two quaternary aromatic C atoms of the benzene ring (C16 and C21, respectively).

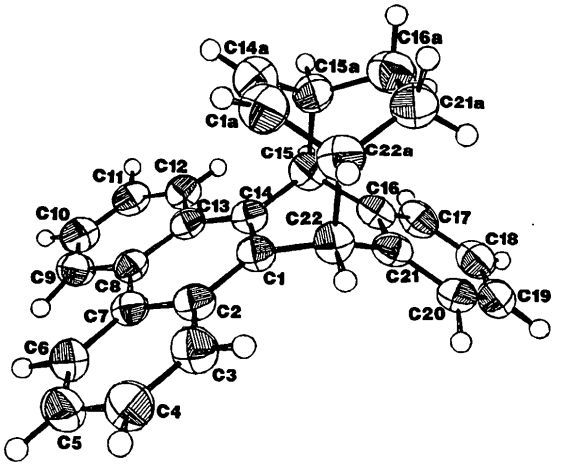

Fig. 1. *ORTEP* representation of the title compound with 50% probability ellipsoids and showing the atom-numbering scheme.

Experimental

Crystal data

$C_{28}H_{22}$
M_r = 358.48
Monoclinic
$P2_1/n$
a = 10.472 (5) Å
b = 11.279 (6) Å
c = 16.358 (8) Å
β = 104.45 (4)°
V = 1871 (3) Å^3
Z = 4
D_x = 1.273 Mg m^{-3}
D_m = 1.25 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.70926 Å
Cell parameters from 25 reflections
θ = 4.15–9.69°
μ = 0.067 mm^{-1}
T = 298 K
Irregular
0.37 × 0.34 × 0.20 mm
Yellowish, transparent
Crystal source: methanol–dichloromethane

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
T_{min} = 0.827,
T_{max} = 0.998
3694 measured reflections
3119 independent reflections
1528 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.038
θ_{max} = 25.0°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 150 min
intensity variation: 0.2%

Refinement

Refinement on F
Final R = 0.053
wR = 0.061
S = 1.735
1528 reflections
254 parameters
$w = 4(F_o)^2/[\sigma(F_o)^2]^2$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.165 e Å^{-3}
$\Delta\rho_{min}$ = −0.187 e Å^{-3}
Extinction correction: $F_c = F_c/(1 + gI_c)$
Extinction coefficient: 4.62 ×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
C1	0.0522 (3)	0.8683 (3)	0.6905 (2)	3.37 (8)
C1*a*	−0.0484 (4)	0.6679 (4)	0.5973 (3)	5.0 (1)
C2	−0.0511 (3)	0.9490 (3)	0.6976 (2)	3.42 (8)
C3	−0.1210 (3)	1.0197 (4)	0.6300 (2)	4.21 (9)
C4	−0.2156 (4)	1.0972 (4)	0.6376 (2)	4.6 (1)
C5	−0.2488 (4)	1.1098 (3)	0.7141 (3)	4.7 (1)
C6	−0.1846 (4)	1.0417 (3)	0.7819 (2)	4.18 (9)
C7	−0.0882 (3)	0.9590 (3)	0.7756 (2)	3.33 (8)
C8	−0.0222 (3)	0.8840 (3)	0.8459 (2)	3.19 (8)
C9	−0.0576 (4)	0.8868 (3)	0.9239 (2)	4.18 (9)
C10	0.0041 (4)	0.8151 (3)	0.9898 (2)	4.7 (1)
C11	0.1019 (4)	0.7381 (4)	0.9806 (2)	4.45 (9)
C12	0.1395 (3)	0.7324 (3)	0.9064 (2)	4.00 (9)
C13	0.0769 (3)	0.8040 (3)	0.8363 (2)	3.28 (8)
C14*a*	0.0109 (4)	0.5997 (4)	0.6612 (2)	5.1 (1)
C14	0.1142 (3)	0.7977 (3)	0.7564 (2)	3.29 (8)
C15	0.2179 (4)	0.7124 (3)	0.7410 (2)	4.00 (9)
C15*a*	0.1568 (4)	0.5972 (3)	0.6872 (2)	4.49 (9)
C16*a*	0.2079 (4)	0.5760 (4)	0.6080 (3)	5.2 (1)
C16	0.3097 (3)	0.7816 (3)	0.7006 (2)	3.63 (8)
C17	0.4444 (3)	0.7811 (3)	0.7277 (2)	4.20 (9)
C18	0.5197 (4)	0.8526 (4)	0.6887 (2)	4.8 (1)
C19	0.4581 (4)	0.9257 (3)	0.6231 (2)	4.7 (1)
C20	0.3238 (3)	0.9263 (3)	0.5953 (2)	3.87 (9)
C21	0.2468 (4)	0.8550 (3)	0.6328 (2)	3.57 (8)
C21*a*	0.1383 (4)	0.6564 (4)	0.5330 (3)	5.1 (1)
C22*a*	0.0363 (3)	0.7397 (3)	0.5553 (2)	4.34 (9)
C22	0.0980 (3)	0.8545 (3)	0.6096 (2)	3.59 (8)

Table 2. *Geometric parameters* (Å, °)

C1—C2	1.441 (5)	C12—C13	1.423 (5)
C1—C14	1.367 (4)	C13—C14	1.455 (5)
C1—C22	1.523 (5)	C14*a*—C15*a*	1.480 (5)

C1*a*—C14*a*	1.322 (5)	C14—C15	1.518 (5)
C1*a*—C22*a*	1.489 (6)	C15—C15*a*	1.610 (5)
C2—C3	1.412 (5)	C15—C16	1.513 (5)
C2—C7	1.427 (5)	C15*a*—C16*a*	1.537 (6)
C3—C4	1.350 (5)	C16*a*—C21*a*	1.555 (5)
C4—C5	1.387 (6)	C16—C17	1.367 (5)
C5—C6	1.378 (5)	C16—C21	1.410 (5)
C6—C7	1.397 (5)	C17—C18	1.388 (6)
C7—C8	1.457 (4)	C18—C19	1.380 (5)
C8—C9	1.414 (5)	C19—C20	1.366 (5)
C8—C13	1.414 (5)	C20—C21	1.385 (5)
C9—C10	1.374 (5)	C21—C22	1.509 (5)
C10—C11	1.380 (6)	C21*a*—C22*a*	1.534 (6)
C11—C12	1.367 (5)	C22*a*—C22	1.612 (5)
C2—C1—C14	121.5 (3)	C1—C14—C15	117.1 (3)
C2—C1—C22	122.7 (3)	C13—C14—C15	122.9 (3)
C14—C1—C22	115.8 (3)	C14—C15—C15*a*	113.5 (3)
C14*a*—C1*a*—C22*a*	117.7 (3)	C14—C15—C16	107.8 (3)
C1—C2—C3	123.1 (3)	C15*a*—C15—C16	112.8 (3)
C1—C2—C7	120.0 (3)	C14*a*—C15*a*—C15	112.5 (3)
C3—C2—C7	116.9 (3)	C14*a*—C15*a*—C16*a*	108.2 (3)
C2—C3—C4	122.8 (4)	C15—C15*a*—C16*a*	114.3 (3)
C3—C4—C5	120.3 (3)	C15*a*—C16*a*—C21*a*	112.4 (3)
C4—C5—C6	119.2 (4)	C15—C16—C17	125.0 (3)
C5—C6—C7	121.9 (4)	C15—C16—C21	115.0 (3)
C2—C7—C6	118.9 (3)	C17—C16—C21	119.9 (3)
C2—C7—C8	118.6 (3)	C16—C17—C18	120.4 (3)
C6—C7—C8	122.6 (3)	C17—C18—C19	119.7 (3)
C7—C8—C9	121.3 (3)	C18—C19—C20	120.3 (4)
C7—C8—C13	119.9 (3)	C19—C20—C21	120.9 (3)
C9—C8—C13	118.7 (3)	C16—C21—C20	118.7 (3)
C8—C9—C10	121.1 (4)	C16—C21—C22	116.5 (3)
C9—C10—C11	120.0 (4)	C20—C21—C22	124.7 (3)
C10—C11—C12	120.9 (3)	C16*a*—C21*a*—C22*a*	112.8 (3)
C11—C12—C13	120.8 (3)	C1*a*—C22*a*—C21*a*	107.9 (3)
C8—C13—C12	118.4 (3)	C1*a*—C22*a*—C22	112.7 (3)
C8—C13—C14	120.0 (3)	C21*a*—C22*a*—C22	114.6 (3)
C12—C13—C14	121.6 (3)	C1—C22—C21	108.1 (3)
C1*a*—C14*a*—C15*a*	119.1 (4)	C1—C22—C22*a*	113.0 (3)
C1—C14—C13	119.9 (3)	C21—C22—C22*a*	112.9 (3)
C1—C22—C22*a*—C1*a*	−2.3	C21—C22—C22*a*—C21*a*	−3.3
C14—C15—C15*a*—C14*a*	1.6	C16—C15—C15*a*—C16*a*	2.9

Plane (1)	Plane (2)	Dihedral angle
C1-C14	C16-C21	53.9
C15*a*, C16*a*, C21*a*, C22*a*	C1*a*, C14*a*, C15*a*, C22*a*	52.6

Crystals were grown from a solution of dichloromethane and methanol by slow evaporation. A suitable single crystal was attached to the end of a glass fiber using fast-drying epoxy glue. The intensity data were corrected for empirical absorption (ψ scans) (North, Phillips & Mathews, 1968), Lorentz and polarization effects and secondary extinction. The structure was solved by direct methods and subsequent difference Fourier maps. All C atoms were refined anisotropically. The H atoms were located on difference electron density maps or generated in chemically reasonable positions and were not refined. All calculations were performed using a PDP-11 minicomputer and Enraf-Nonius *SDP-Plus* software (B. A. Frenz & Associates, Inc., 1983).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71298 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1050]

References

B. A. Frenz & Associates, Inc. (1983). *SDP-Plus Structure Determination Package*. College Station, Texas, USA, and Enraf–Nonius, Delft, The Netherlands.

Dougherty, D. A., Hounshell, W. D., Schlegel, H. B., Bell, R. A. & Mislow, K. (1976). *Tetrahedron Lett.* **39**, 3479–3482.

Ehrenberg, M. (1966). *Acta Cryst.* **20**, 177–182, 182–186.

Ehrenberg, M. (1968). *Acta Cryst.* B**24**, 1123–1125.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Yang, N. C., Gan, H., Kim, S. S., Masnovi, J., Rafalko, P. W., Ezell, E. F. & Lenz, G. R. (1990). *Tetrahedron Lett.* **31**, 3825–3828.

Yang, N. C., Masnovi, J., Chiang, W., Wang, T., Shou, H. & Yang, D. D. H. (1981). *Tetrahedron*, **37**, 3285–3300.

Acta Cryst. (1993). C**49**, 1965–1967

6,7,8,9-Tetrahydro-4-methyl-2*H*-pyrano-[3,2-*g*]quinolin-2-one

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Abstract

In the title compound, also known as coumarin 339, the coumarin moiety is planar and coplanar with the methyl group at C4 [C2—C3—C4—C12 = 179.9 (2) and C9—C10—C4—C12 = 178.4 (2)°]. The structure is stabilized by extensive intermolecular C—O···H hydrogen bonding.

Comment

The title compound, a laser dye, has been used in novel polymeric environments (Jones & Ragman, 1990), as well as in singlet excitation-energy correlation chemiluminescence reactions (Tod, Farinotti, Mahuzier & Gaury, 1989). The benzene and pyrone rings are planar (χ^2 = 24.5 and 88.2) and the dihedral angle between the rings is 1.57°.

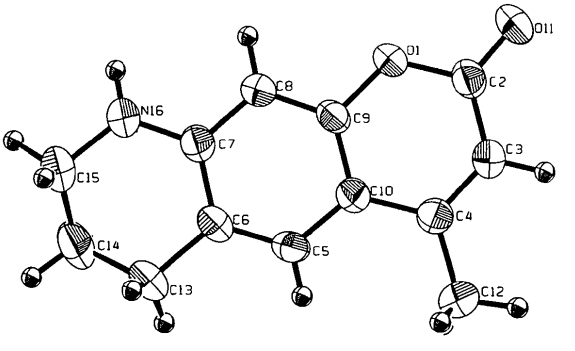

Fig. 1. *ORTEP* (Johnson, 1976) drawing (50% probability ellipsoids) and atomic numbering scheme.