

(±)-7,10,12-Triphenyl-7,8-dihydroacenaphtho[4,5-c]quinolizinium Perchlorate

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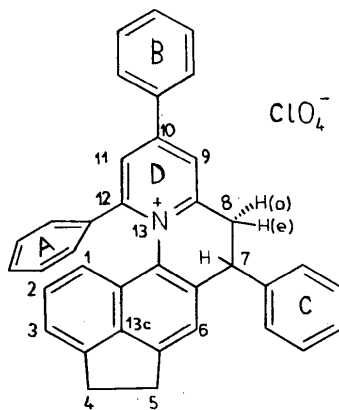
Abstract. $C_{37}H_{28}N^+ClO_4^-$, $M_r = 586.09$, triclinic, $P\bar{1}$, $a = 11.738$ (8), $b = 12.879$ (10), $c = 11.027$ (5) Å, $\alpha = 111.89$ (5), $\beta = 110.28$ (10), $\gamma = 91.19$ (7)°, $V = 1429.3$ Å³, $Z = 2$, $D_x = 1.362$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.710690$ Å, $\mu = 0.173$ mm⁻¹, $F(000) = 612$, $T = 293$ K, $R = 0.0504$, $wR = 0.0479$ for 3256 reflections. The aromaticity of the rings is discussed. The A and C rings of the molecule are on the same side of the best plane through the molecule. The unsaturated six-membered ring has a twist-boat conformation.

Experimental. Crystals for diffraction analysis were grown in nitromethane solution. Their melting point is 572–573 K. A crystal of dimensions $0.35 \times 0.35 \times 0.35$ mm was used for data collection. A KM4 KUMA diffractometer was used with graphite-monochromatized Mo $K\alpha$ radiation. Unit-cell parameters were obtained by least-squares fit of the setting angles of 25 reflections in the range $10 \leq \theta \leq 30^\circ$. The intensities of 5788 reflections were measured with ω - 2θ scans; index range $-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $l \leq 11$; $(\sin\theta)/\lambda \leq 1.21$ Å⁻¹. The data were

< 5%. Of 4631 measured reflections, 3256 with $F_o \geq 3\sigma(F_o)$ were used in the calculations; $R_{\text{int}} = 0.0455$. The structure was solved by direct methods. Block-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ with weights $w = 3.0129[\sigma^2(F_o) + 0.0001(F_o)^2]^{-1}$ was employed. Heavy atoms were refined anisotropically and all H atoms were obtained from a $\Delta\rho$ map and refined with isotropic displacement parameters. For the ClO_4^- anion eight O-atom positions were found. Their site occupancies were fixed at values given in Table 1. Final $R = 0.0504$, $wR = 0.0479$, $S = 4.871$ for 3256 reflections and 528 parameters; the final difference Fourier map showed $\Delta\rho_{\text{max}} = +0.20$, $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³. $(\Delta/\sigma)_{\text{max}} = 0.021$ in the final cycle, average $\Delta/\sigma = 0.009$. The computer programs *SHELXS86* (Sheldrick, 1990) and *SHELX76* (Sheldrick, 1976) were used. The final geometric calculations were performed with the program *CSU* (Vickovic, 1988). Molecular illustrations were drawn using *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

The final atomic parameters are given in Table 1,* selected distances and angles are presented in Table 2. A stereoscopic view of the molecule with the atom-numbering scheme is shown in Fig. 1.

Related literature. The title compound was prepared by photochemical cyclization of 1-(acenaphth-5-yl)-2-styryl-4,6-diphenylpyridinium perchlorate which is a hemicyanine-like dye. This process was carried out in methanol solution using light from a high-pressure mercury arc lamp (Soroka, 1992). The primary photoproduct, (±)-7,10,12-triphenyl-6a,7-dihydro-



corrected for Lorentz and polarization effects but no absorption correction was applied; three reflections (211, 222, 10 $\bar{1}$) were monitored every 100 reflections. The variation of the intensity control reflections was

* Lists of structure factors, anisotropic thermal parameters, bond lengths, bond angles, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55278 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0257]

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$B_{\text{eq}} = 8\pi^2 D_u^{1/3} / [\sin\alpha^* \sin\beta^* \sin\gamma^*]^2$$

	x	y	z	B_{eq}
N(1)	0.3367 (1)	0.3376 (1)	0.3594 (2)	3.18 (4)
C(2)	0.3424 (2)	0.2323 (2)	0.2664 (2)	3.16 (5)
C(3)	0.4290 (2)	0.1729 (2)	0.3156 (2)	3.60 (6)
C(4)	0.5035 (2)	0.2093 (2)	0.4587 (2)	3.84 (6)
C(5)	0.4827 (2)	0.3085 (2)	0.5503 (2)	3.91 (5)
C(6)	0.4009 (2)	0.3717 (2)	0.5031 (2)	3.59 (5)
C(7)	0.3666 (2)	0.4742 (2)	0.5954 (2)	4.06 (5)
C(8)	0.2269 (2)	0.4713 (2)	0.5305 (2)	3.58 (6)
C(9)	0.2057 (2)	0.4800 (2)	0.3916 (2)	3.50 (5)
C(10)	0.2693 (2)	0.4175 (1)	0.3124 (2)	3.12 (5)
C(11)	0.2801 (2)	0.4391 (1)	0.1990 (2)	3.17 (5)
C(12)	0.3569 (2)	0.3984 (2)	0.1231 (2)	3.48 (5)
C(13)	0.3601 (2)	0.4380 (2)	0.0246 (3)	4.27 (3)
C(14)	0.2872 (2)	0.5163 (2)	-0.0091 (3)	4.39 (7)
C(15)	0.2118 (2)	0.5573 (2)	0.0615 (2)	3.87 (6)
C(16)	0.2104 (2)	0.5194 (2)	0.1656 (2)	3.37 (5)
C(17)	0.1374 (2)	0.5773 (2)	0.2384 (2)	3.67 (5)
C(18)	0.1364 (2)	0.5589 (2)	0.3512 (3)	3.83 (6)
C(19)	0.1253 (3)	0.6419 (2)	0.0540 (3)	4.62 (7)
C(20)	0.0785 (3)	0.6571 (2)	0.1731 (3)	4.53 (7)
C(21)	0.2468 (2)	0.1802 (1)	0.1204 (2)	3.19 (5)
C(22)	0.2799 (2)	0.1192 (2)	0.0083 (2)	3.99 (6)
C(23)	0.1896 (3)	0.0638 (2)	-0.1249 (3)	4.73 (6)
C(24)	0.0672 (3)	0.0660 (2)	-0.1476 (3)	5.07 (6)
C(25)	0.0338 (2)	0.1245 (2)	-0.0361 (3)	4.63 (6)
C(26)	0.1233 (2)	0.1816 (2)	0.0974 (3)	3.90 (5)
C(41)	0.5901 (2)	0.1381 (2)	0.5076 (3)	4.09 (7)
C(42)	0.6371 (3)	0.0643 (3)	0.4174 (4)	5.33 (14)
C(43)	0.7111 (3)	-0.0090 (3)	0.4583 (4)	5.99 (20)
C(44)	0.7390 (3)	-0.0077 (3)	0.5893 (4)	5.43 (10)
C(45)	0.6960 (3)	0.0667 (3)	0.6821 (4)	5.20 (8)
C(46)	0.6218 (2)	0.1399 (2)	0.6426 (3)	4.65 (6)
C(81)	0.1480 (2)	0.3686 (2)	0.5185 (2)	3.41 (6)
C(82)	0.1839 (3)	0.3274 (2)	0.6228 (3)	4.63 (7)
C(83)	0.1089 (3)	0.2375 (2)	0.6140 (4)	5.26 (13)
C(84)	-0.0004 (3)	0.1878 (2)	0.5014 (4)	5.36 (10)
C(85)	-0.0382 (3)	0.2278 (2)	0.3965 (3)	4.95 (7)
C(86)	0.0359 (2)	0.3179 (2)	0.4057 (2)	4.02 (6)
Cl	0.6412 (1)	0.2063 (1)	0.0758 (1)	5.53 (3)
O(1)†	0.7551 (4)	0.1975 (7)	0.0695 (7)	8.53 (38)
O(2)†	0.6147 (8)	0.1871 (13)	0.1751 (10)	10.40 (60)
O(3)†	0.6329 (11)	0.3070 (5)	0.1565 (9)	8.98 (30)
O(4)†	0.5550 (8)	0.1921 (13)	-0.0545 (7)	9.22 (26)
O(5)†	0.7503 (12)	0.3012 (10)	0.1621 (9)	8.10 (3)
O(6)†	0.5613 (11)	0.2638 (13)	0.0154 (20)	9.22 (60)
O(7)†	0.6441 (27)	0.1198 (10)	-0.0265 (16)	13.50 (85)
O(8)†	0.6121 (10)	0.1259 (6)	0.1160 (14)	9.01 (80)

† Site occupancies: O(1) 0.7, O(2) 0.6, O(3) 0.5, O(4) 0.6, O(5) 0.3, O(6) 0.4, O(7) 0.4, O(8) 0.5.

acenaphtho[4,5-*c*]quinolizinium perchlorate had been catalyzed by two independent [1,5] H-shift mechanisms: one of them is a one-step sigmatropic and the other a two-step weak base catalysis. The acenaphtho[4,5-*c*]quinolizinium skeleton has not previously been reported in the literature.

The torsion angles (Table 2) and the calculated asymmetry parameters (Duax & Norton, 1975) for the unsaturated six-membered ring [N(1)—C(6)—C(7)—C(8)—C(9)—C(10)] indicate a twist-boat conformation with the asymmetry parameter $\Delta C_2^{6-9} = 26.2^\circ$. The rings connected to the molecule by single C—C bonds are more aromatic than those condensed by more links as indicated by the aromaticity

Table 2. Selected bond lengths (\AA) and torsion angles ($^\circ$)

C(2)—N(1)	1.382 (3)	C(18)—C(9)	1.419 (4)
C(6)—N(1)	1.382 (3)	C(11)—C(10)	1.423 (4)
C(10)—N(1)	1.449 (2)	C(12)—C(11)	1.416 (4)
C(3)—C(2)	1.368 (4)	C(16)—C(11)	1.409 (3)
C(21)—C(2)	1.487 (2)	C(13)—C(12)	1.372 (5)
C(4)—C(3)	1.396 (3)	C(14)—C(13)	1.408 (4)
C(5)—C(4)	1.391 (3)	C(15)—C(14)	1.363 (4)
C(41)—C(4)	1.481 (4)	C(16)—C(15)	1.410 (4)
C(6)—C(5)	1.363 (4)	C(19)—C(15)	1.510 (4)
C(7)—C(6)	1.498 (3)	C(17)—C(16)	1.411 (3)
C(8)—C(7)	1.538 (3)	C(18)—C(17)	1.354 (4)
C(9)—C(8)	1.512 (4)	C(20)—C(17)	1.513 (4)
C(81)—C(8)	1.536 (4)	C(20)—C(19)	1.542 (5)
C(10)—C(9)	1.386 (3)		
N(1)—C(6)—C(7)—C(8)	37.1 (4)	C(26)—C(21)—C(2)—C(3)	128.3 (3)
C(6)—C(7)—C(8)—C(9)	-64.0 (3)	C(42)—C(41)—C(4)—C(3)	27.2 (4)
C(7)—C(8)—C(9)—C(10)	41.5 (2)	C(46)—C(41)—C(4)—C(3)	-149.9 (2)
C(8)—C(9)—C(10)—C(1)	8.4 (2)	C(42)—C(41)—C(4)—C(5)	-158.9 (3)
C(9)—C(10)—C(1)—C(6)	-41.0 (3)	C(46)—C(41)—C(4)—C(5)	24.0 (4)
C(10)—C(1)—C(6)—C(7)	15.5 (3)	C(82)—C(81)—C(8)—C(7)	37.6 (3)
C(22)—C(21)—C(2)—C(1)	142.3 (2)	C(86)—C(81)—C(8)—C(7)	-145.4 (2)
C(26)—C(21)—C(2)—C(1)	-44.8 (3)	C(82)—C(81)—C(8)—C(9)	157.9 (2)
C(22)—C(21)—C(2)—C(3)	-44.6 (4)	C(86)—C(81)—C(8)—C(9)	-25.1 (3)

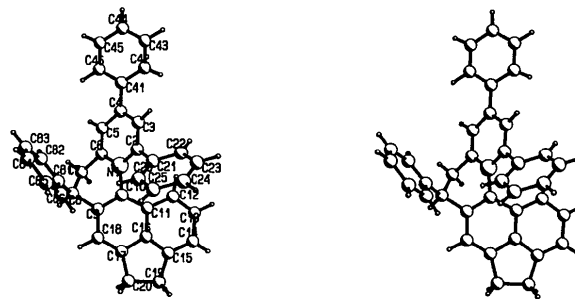


Fig. 1. A stereoview showing the atom numbering.

index HOMA* (Kruszewski & Krygowski, 1972; Gdaniec, Turowska-Tyrk & Krygowski, 1989). HOMA applied to the first type of ring gives values between 0.939 (ring *B*) and 0.979 (ring *C*). The other rings have HOMA values 0.813 (ring *D*) and 0.803 and 0.871 for the rings in the naphthalene moiety.

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* HOMA = $1 - a/n \sum_{i=1}^n (R_{\text{opt}} - R_i)^2$, where R_{opt} is the C—C bond length for which the harmonic oscillator energies for extension to the single-bond length and compression to the double-bond length are equal. $R_{\text{opt}} = 1.388$ and $a = 257.7$ gives HOMA = 1 for all bonds equal to 1.388 and HOMA = 0 for the Kekulé structure with $R(\text{C—C}) = 1.469$ Å and $R(\text{C=C}) = 1.349$ Å (bond lengths of 1,3-butadiene).

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Structures of Three Tetrahydrofurofuran-Type Lignanes

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Abstract. (1) (+)-Pinoresinol, 1-hydroxy-4,4'-diacetate monohydrate {4,4'-(tetrahydro-1-hydroxy-1*H*,-3*H*-furo[3,4-*c*]furan-1,4-diyl)bis(2-methoxyphenyl) diacetate monohydrate}, C₂₄H₂₆O₉.H₂O, *M_r* = 476.5, orthorhombic, *P*2₁2₁2₁, *a* = 7.230 (2), *b* = 7.702 (1), *c* = 42.420 (5) Å, *V* = 2362.2 (11) Å³, *Z* = 4, *D_x* = 1.340 g cm⁻³, *Cu Kα*, λ = 1.54184 Å, μ = 8.4 cm⁻¹, *F*(000) = 1008, *T* = 297 K, *R* = 0.043 for 3834 observations with *I* > 3σ(*I*) (of 4808 unique data). The two five-membered rings of the central dioxabicyclo-octane system are *cis*-fused, each ring adopting the half-chair conformation with the C atom not carrying the OH group lying on both pseudodiads. The phenyl rings are planar with maximum deviations 0.006 (2) and 0.008 (2) Å, and the two methoxy substituents lie near these planes, with C—C—O—C torsion angles of 7.1 (4) and 2.7 (4)°. The acetate substituents are more nearly orthogonal to the phenyl rings, with C—C—O—C torsion angles of 87.2 (3) and 73.4 (3)°. The OH group donates a hydrogen bond to the water molecule, with O...O distance of 2.795 (3) Å and angle at H of 165 (3)°. (2) Yangambin {tetrahydro-1,4-bis(3,4,5-trimethoxyphenyl)-1*H*,3*H*-furo[3,4-*c*]furan}, C₂₄H₃₀O₈, *M_r* = 446.5, orthorhombic, *P*2₁2₁2₁, *a* = 5.5333 (5), *b* = 12.5520 (7), *c* = 31.723 (2) Å, *V* = 2203.2 (5) Å³, *Z* = 4, *D_x* = 1.346 g cm⁻³, *Cu Kα*, λ = 1.54184 Å, μ = 8.0 cm⁻¹, *F*(000) = 952, *T* = 299 K, *R* = 0.028 for 4311 observations having *I* > 3σ(*I*) (of 4514 unique data). The two five-membered rings of yangambin are *cis*-fused with envelope conformations, with the O atoms at the flap positions. Maximum deviations from planarity are 0.0014 (12) Å for one phenyl sub-

stituent and 0.0156 (11) Å for the other. Both phenyl groups carry three methoxy groups, one of the three *para* to the tetrahydrofuran and the other two *meta* to tetrahydrofuran. The *para* methoxy groups are rotated out of the phenyl planes, with C—C—O—C torsion angles of 72.90 (14) and 79.83 (14)°, while the *meta* methoxy groups are more nearly coplanar with the phenyl rings, with analogous magnitudes ranging 0.0 (5)–6.1 (2)°. (3) (–)-Asarinin (episesamin) {5,5'-(tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan-1,4-diyl)bis(1,3-benzodioxole)}, C₂₀H₁₈O₆, *M_r* = 354.4, monoclinic, *P*2₁, *a* = 9.6127 (10), *b* = 5.6194 (4), *c* = 15.660 (2) Å, β = 103.687 (7)°, *V* = 821.9 (3) Å³, *Z* = 2, *D_x* = 1.432 g cm⁻³, *Cu Kα*, λ = 1.54184 Å, μ = 8.4 cm⁻¹, *F*(000) = 372, *T* = 297 K, *R* = 0.030 for 1761 observations with *I* > 3σ(*I*) (of 1829 unique data). Unlike the other two compounds, which have both phenyl substituents *cis* to bridgehead H and thus *syn* to each other, asarinin has its two phenyl substituents *anti* to each other. The fused five-membered rings have the same envelope conformation as those of yangambin. The phenyl rings exhibit maximum deviations from planarity of 0.003 (2) and 0.004 (2) Å. One ketal ring is nearly coplanar with the phenyl group to which it is fused, its methylene C atom lying only 0.012 (3) Å out of the plane. The other ketal ring is in an envelope conformation with that C atom 0.220 (3) Å out of the plane.

Experimental. Compound (1) was obtained as colorless needles by acetylation of (+)-1-hydroxypinoresinol from *Calamintha ashei* (Weatherby) Shinner (Lamiaceae). Yangambin (2) was isolated