The C—O bond lengths in the pyrone ring are symmetrical with C7—O2 = 1·352 (5) and C11—O2 = 1·366 (5) Å.

The widening of the angle O2—C7—C6, 124·0 (4)°, and the narrowing of the angle C6—C9—C10, 115·3 (4)°, in ring C may be attributed to the ring strain caused by the neighbouring Csp^2–Csp^2 atoms and has been observed in ethyl 1-cyano-1,2,-3,4-tetrahydro-2-isoquinolinecarboxylate (Gzella, Jaskólski, Rychlewska & Kosturkiewicz, 1984).

The methoxy group attached to ring C is rotated from the plane of the ring about the bond C10—O4 by an angle of 71·6 (6)°. The deviation of C12 from the plane of the ring is 1·226 (8) Å. A similar rotation of the methoxy group has been observed in various structures: celebixanthone, 72·8° (Stout, Stout & Welsh, 1963), 2-hydroxy-1,3,4,7-tetramethoxyxanthone, 72·0, 58·1, 83·0° (Stout, Shunlin & Singh, 1969), xanthone B, 64·0° (Ravikumar, Rajan & Padmanabhan, 1987).

The rings A, B and D are planar ($\chi^2 = 1·0$, 8·7 and 29·6 respectively). The pyran ring C is distorted ($\chi^2 = 68·1$). The angles between A and B, A and C, and B and C are 1·1 (2), 3·0 (2) and 2·4 (2)° respectively, showing that the rings A, B and C are coplanar. Similar coplanarity of the phenyl ring B and the pyrone ring C has been observed in 3′,5,5′,6-tetramethoxyflavone (Ting, Watson & Dominguez, 1972). The rotation of the phenyl ring D through 28·7 (2)° from the plane of the pyran ring may be to minimize the steric interaction between the oxygen atom O2 in the pyrone ring and O4 of the methoxy group with the phenyl ring D. This is substantiated by the distances HC18···O2 and HC14···O4, 2·36 (6) and 2·36 (5) Å respectively, which are less than 2·62 Å, the sum of the van der Waals radii of the H and O atoms (Srinivasan, Meena Hariharan & Vijaya-lakshmi, 1987; Nyburg & Faerman, 1985).

A stereoview of the unit-cell packing (Motherwell, 1978) is shown in Fig. 3. The molecules are stacked along the a axis with C7···C8 $(1 - x, -y, 1 - z)$ being 3·494 (7) Å. The structure is stabilized by C—H···O-type contacts and stacking forces. C14 is linked by a hydrogen bond to O4 $(1 - x, 1 - y, 1 - z)$ with C14···O4 3·285 (7), C14—HC14 1·01 (6) Å and angle C14—HC14···O4 137 (4)°. There is another C···O contact, between C4 and O3 $(\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z)$, with C4···O3 3·294 (7) Å. The molecules lie approximately in the bc plane.

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Structure of Dicyclopenta[ef,kl]heptalene (Azupyrene)

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Abstract. $C_{16}H_{10}$, $M_r = 202·255$, monoclinic, $P2_1/c$, $a = 8·356 (1)$, $b = 11·076 (3)$, $c = 11·446 (2)$ Å, $\beta = 104·91 (1)°$, $V = 1023·8 (7)$ Å^3, $Z = 4$, $D_x = 1·312$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·692$ cm^{-1}, $F(000) = 424$, $T = 298$ (1) K, $R = 0·055$ for 961 observed reflections. The molecule is planar with slight perimeter bond-length alternation, primarily in the five-carbon-ring moieties. The lengths of

Table 1. *Positional and equivalent isotropic thermal parameters for* $C_{16}H_{10}$

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i.\mathbf{a}_j$, where the $\mathbf{a}_i$'s are the lattice vectors in direct space.

	x	y	z	B_{eq} (Å²)
C(1)	0·1326 (4)	−0·0436 (3)	0·2511 (3)	5·51 (9)
C(2)	0·2457 (5)	0·0379 (3)	0·2318 (3)	6·0 (1)
C(2A)	0·4100 (4)	0·0041 (3)	0·2961 (3)	4·83 (8)
C(3)	0·5502 (5)	0·0669 (3)	0·2942 (3)	6·2 (1)
C(4)	0·7125 (5)	0·0395 (3)	0·3484 (3)	5·96 (9)
C(5)	0·7752 (4)	−0·0552 (3)	0·4222 (3)	5·54 (9)
C(5A)	0·6939 (4)	−0·1473 (3)	0·4601 (3)	4·48 (8)
C(6)	0·7717 (4)	−0·2407 (4)	0·5411 (3)	5·62 (9)
C(7)	0·6590 (5)	−0·3183 (3)	0·5641 (3)	5·44 (9)
C(7A)	0·4977 (5)	−0·2844 (3)	0·5015 (3)	4·72 (8)
C(8)	0·3563 (5)	−0·3456 (3)	0·5057 (3)	5·8 (1)
C(9)	0·1942 (4)	−0·3214 (3)	0·4459 (3)	5·95 (9)
C(10)	0·1293 (4)	−0·2305 (4)	0·3675 (3)	5·8 (1)
C(10A)	0·2107 (4)	−0·1371 (3)	0·3297 (3)	4·38 (8)
C(11)	0·3918 (4)	−0·1094 (3)	0·3609 (3)	4·34 (8)
C(12)	0·5143 (4)	−0·1726 (3)	0·4325 (3)	4·26 (8)

Table 2. *Bond distances* (Å) *and angles* (°) *for* $C_{16}H_{10}$

C(1)—C(2)	1·365 (5)	C(6)—C(7)	1·350 (4)
C(1)—C(10A)	1·415 (4)	C(7)—C(7A)	1·405 (4)
C(2)—C(2A)	1·431 (4)	C(7A)—C(8)	1·373 (4)
C(2A)—C(3)	1·367 (4)	C(7A)—C(12)	1·494 (4)
C(2)—C(11)	1·488 (4)	C(8)—C(9)	1·378 (4)
C(3)—C(4)	1·372 (5)	C(9)—C(10)	1·364 (4)
C(4)—C(5)	1·364 (4)	C(10)—C(10A)	1·368 (4)
C(5)—C(5A)	1·358 (4)	C(10A)—C(11)	1·495 (4)
C(5A)—C(6)	1·429 (4)	C(11)—C(12)	1·333 (3)
C(5A)—C(12)	1·478 (4)		

C(2)—C(1)—C(10A)	111·2 (3)	C(7)—C(7A)—C(12)	106·4 (3)
C(1)—C(2)—C(2A)	110·9 (3)	C(8)—C(7A)—C(12)	128·7 (3)
C(2)—C(2A)—C(3)	124·9 (3)	C(7A)—C(8)—C(9)	129·1 (3)
C(2)—C(2A)—C(11)	105·7 (3)	C(8)—C(9)—C(10)	130·1 (3)
C(3)—C(2A)—C(11)	129·5 (3)	C(9)—C(10)—C(10A)	128·3 (3)
C(2A)—C(3)—C(4)	129·2 (4)	C(1)—C(10A)—C(10)	124·7 (3)
C(3)—C(4)—C(5)	128·9 (4)	C(1)—C(10A)—C(11)	106·0 (3)
C(4)—C(5)—C(5A)	129·2 (3)	C(10)—C(10A)—C(11)	129·4 (3)
C(5)—C(5A)—C(6)	124·7 (3)	C(2A)—C(11)—C(10A)	106·3 (2)
C(5)—C(5A)—C(12)	129·7 (3)	C(2A)—C(11)—C(12)	126·1 (3)
C(6)—C(5A)—C(12)	105·6 (3)	C(10A)—C(11)—C(12)	127·6 (3)
C(5A)—C(6)—C(7)	111·3 (3)	C(5A)—C(12)—C(7A)	105·8 (2)
C(6)—C(7)—C(7A)	110·9 (3)	C(5A)—C(12)—C(11)	127·5 (3)
C(7)—C(7A)—C(8)	124·9 (3)	C(7A)—C(12)—C(11)	126·8 (3)

the four C—C bonds connecting the internal ethylene unit to the perimeter range from 1·478 (4) to 1·495 (4) Å. The internal ethylene unit must be considered isolated with little or no interaction with the annulene-like perimeter.

Introduction. The title compound was conceived and selected for synthesis (Anderson, MacDonald & Montana, 1968) to provide a definitive test of the theory of concentric orbital nodes (Platt, 1954) separating a $4n + 2$ π-electron molecular periphery from internal π electrons to achieve the energetic stability associated with so-called aromatic compounds. Prior to this, no totally nonbenzenoid (necessary to preclude stabilization by benzenoid moieties as in pyrene), conjugate-unsaturated hydrocarbon having the requisite structure was known.

Critical to the objective was the determination of the bond lengths and bond angles in the molecule. Earlier attempts to obtain a suitable crystal of the parent molecule or of various derivatives (Anderson, Daugs & Kao, 1988, and references therein) were unsuccessful.

Experimental. A dark greenish-brown plate from slow evaporation of hexane, $0·66 \times 0·65 \times 0·03$ mm, mounted on a glass filament along an edge, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, lattice parameters from 25 reflections with $30 < 2\theta < 36·5°$, max. $(\sin\theta)/\lambda = 0·5941$ Å⁻¹, three standard reflections measured every 80 reflections with $\theta \sim 23$–26°, max. variation 9·6%, decay $= -4·5\%$ (linear correction), 2034 reflections in two octants ($h: 0\rightarrow9$, $k: 0\rightarrow13$, $l: -13 \rightarrow13$) with $2\theta < 50°$, ω-2θ scan, scan rate $= 2°$ min⁻¹, range $\Delta\theta = 0·90° + 0·347°\tan\theta$, 1898 averaged reflections in $P2_1/c$, $R_{av} = 0·035$ on F_{obs}, 961
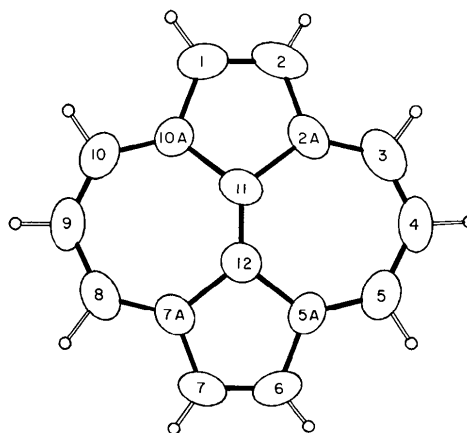

Fig. 1. *ORTEP* drawing of azupyrene. Thermal ellipsoids for C atoms are drawn at a probability of 0·40; H atoms are on an arbitrary scale.
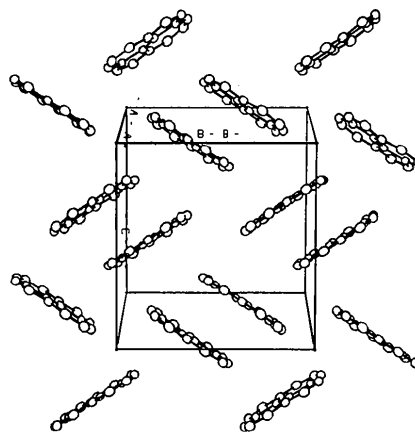

Fig. 2. *ORTEP* view of the unit cell. Thermal ellipsoids for C at 0·20 probability. H atoms omitted.

unique reflections with $I > 3\sigma(I)$, no absorption correction, direct methods, refinement by full-matrix least squares on F, all non-H atoms anisotropic, all H atoms isotropic and initially located by calculation, 185 parameters refined, max. shift/e.s.d. = 0·00 on final cycle, $R = 0.055$, $wR = 0.063$, GOF = 1·894, $w^{-1} = [\sigma^2_{count} + (0.04F^2)^2]/4F^2$, final difference map with no features greater than ± 0.3 e Å^{-3}, scattering factors from *International Tables for X-ray Crystallography* (1974), computer programs *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *SDP*/VAX package of programs (Enraf–Nonius, 1979), *ORTEP* (Johnson, 1976).

Discussion. The atomic parameters for the C atoms are listed in Table 1.* The bond distances and angles for the C atoms are given in Table 2. A view of the molecule and the numbering scheme are shown in Fig. 1. A view of the unit cell showing the packing scheme is presented in Fig. 2.

The bond distances and angles are entirely consistent with those expected for a [14]annulene structure with an isolated ethylene unit in the intra-annular space. The molecule is planar within ± 0.04 Å. The four bonds connecting the center two C atoms with the periphery [C(2A)—C(11), C(5A)—C(12), C(7A)—C(12), C(10A)—C(11)] are all decidedly single bond in character with an average length of 1·489 (8) Å. The central bond [C(11)—C(12)] is ethylene-like at 1·333 (3) Å. If π interaction between the central double bond and the aromatic periphery were at all significant, shortening of this first group of four bonds and lengthening of the center bond

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* Tables of anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms, least-squares planes, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52384 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
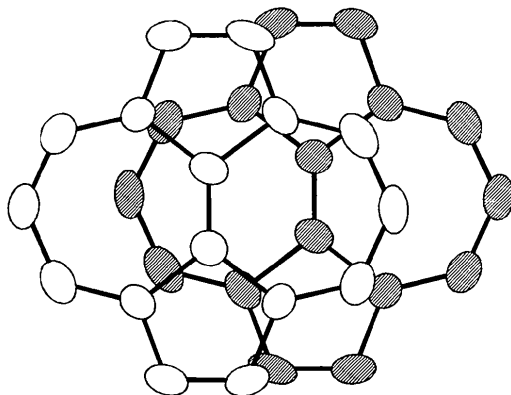

Fig. 3. *ORTEP* view of a pair of molecules viewed perpendicular to the least-squares plane of atoms of the shaded molecule. The viewing distance is infinite.

would be expected. Since this is not observed, it is concluded that π interaction is not indicated. This compound clearly illustrates the principle (Platt, 1954) based on the free-electron model (Bayliss, 1948; Kuhn, 1948; Platt, 1949; Simpson, 1949) that a non-Hückel π system could demonstrate aromatic character if it could be divided into two separate Hückel systems separated by one or more circular nodes. The bond lengths of the peripheral portion of the molecule are consistent with Platt's principle. While there is slight bond-length alternation in the five-membered-ring portions of the periphery, these bonds are still convincingly within the values expected for aromatic C—C bonds.

The molecular stacking (Fig. 2) consists of spatially alternating pairs, related by a center of symmetry, with the five- and seven-membered rings in each molecule of a pair oriented in the same directions (Fig. 3). The average intermolecular distance between the pairs is 3·44 Å. These molecular and crystal structures are not consistent with ones proposed earlier (MacDonald, 1968) whereby the relatively high melting point (533–534 K) of the crystal would be due to internal azulene-like dipoles with partial negative and positive charges in the five- and seven-membered rings respectively, and the molecules in the crystal oriented to maximize the dipolar interactions (Robertson, Shearer, Sim & Watson, 1962). It would appear that such dipoles probably do not exist in azupyrene.

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