and the upper anion of Figs. 3 and 4, supporting the hypothesis of the stacking of charge-transfer dimers. Conversely, no π overlap can occur between the cation and the underlying anion as the S atom, the only one with suitably short contacts, is almost exactly situated over the nodal line through C(10), C(11) and N(5) of the HOMO of the anion. A similar arrangement has been already found by Tamamura *et al.* (1974) in the organic charge-transfer salt between 1,1,3,3-tetracyanopropenide (an anion strictly similar to the present one) and 2,4,6-triphenylpyrylium.

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Structure of Methyl 10-Ethyldicyclohepta[*cd,gh*]pentalene-5-carboxylate, $C_{20}H_{16}O_2$

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Abstract. $M_r = 288\cdot35$, monoclinic, $P2_1/n$, $a = 11\cdot339\,(2)$, $b = 13\cdot423\,(2)$, $c = 10\cdot485\,(1)$ Å, $\beta = 113\cdot80\,(2)^\circ$, $V = 1460\cdot14$ Å^3, $D_x = 1\cdot31$ for $Z = 4$, $D_m = 1\cdot19$ g cm^{-3}, $F(000) = 608$, Mo $K\alpha$ radiation. diffractometer data ($\lambda = 0\cdot71069$ Å, graphite monochromator), $\mu = 0\cdot78$ cm^{-1}, room temperature. The final R factor is 0·073 for the 2563 observed reflections. The molecular skeleton shows a completely planar and 14π peripheral aromatic structure in good agreement with the theoretical prediction. The crystal structure consists of a pair of molecules almost parallel with each other with contacts corresponding to the shorter limits of the van der Waals distances.

Introduction. There are known to exist three nonalternant pyrene isomers fused with only five- and seven-membered rings, dicyclohepta[*cd,gh*]pentalene (1) (Reel & Vogel, 1972), dicyclopenta[*ef,kl*]heptalene (2) (Anderson, MacDonald & Montana, 1968; Jutz & Schweiger, 1971), and pentaleno[6,1,2-*def*]heptalene (3) (Hafner, Fleischer & Fritz, 1965). These types of polycyclic conjugated hydrocarbons are of special interest for their characterization of the 14π peripheral aromatic system, as predicted from quantum mechanical MO calculations (Zahradnik, 1965; Zahradnik, Michel & Pancir, 1966; Toyota & Nakajima, 1973).

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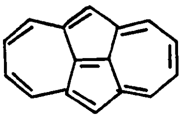
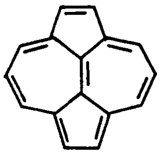


(1)



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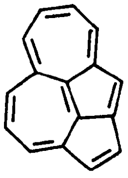
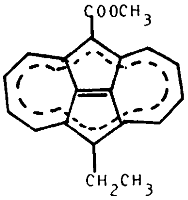


(3)

Since X-ray study has only been reported so far for the 9-methyl derivative of (3) (Linder, 1969), we have undertaken the present study to obtain more structural information on this system. The title compound was chosen because single crystals were isolated among many derivatives having the ring skeleton (1) (Fujimori, Morita, Yasunami, Asao & Takase, 1983).

Experimental. Prism-like brownish green crystals (from a benzene solution), m.p. 446–448 K, $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}25$ mm, D_m by flotation in a mixture of cyclohexane and carbon tetrachloride; Rigaku four-circle diffractometer (AFC-5), graphite-monochromatized Mo $K\alpha$ radiation; unit-cell dimensions by least-squares analysis of 15 reflections with $20° < 2\theta < 40°$; intensity data within $2\theta = 55°$ ($1 \leq h \leq 12$, $0 \leq h \leq 17$, $-12 \leq l \leq 7$) collected by θ–2θ scan mode [scan speed 4° min^{-1} (2θ)]; three standard reflections showed no significant deterioration; Lp corrections, no absorption correction; 3275 independent reflections collected, 2563 reflections with $|F_o| > \sigma|F_o|$ used in the refinement. Direct methods [*MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978)], block-diagonal least-squares refinement: $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(|F_o|)$; all H atoms, except for some methyl hydrogens (whose positions were calculated), were obtained from a difference map and included in the refinement; final $R = 0{\cdot}073$, $R_w = 0{\cdot}075$, $S = 2{\cdot}38$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); $\Delta/\sigma = \sim 0{\cdot}1$, $\Delta\rho$ in final difference map $= -0{\cdot}5 \sim +0{\cdot}5$ e Å^{-3}. ACOS-1000 computer at the Computing Center of Tohoku University; the *Universal Crystallographic Computing System* (1979).

Discussion. The final atomic parameters are given in Table 1.* The bond lengths (uncorrected and corrected for the thermal motion) and bond angles are listed in Table 2. Since the corrections are small ($\simeq 1\sigma$), the following discussion is based on the uncorrected values. The numbering scheme and bond lengths are shown in an *ORTEP* drawing of the molecule (Fig. 1). The 14 perimeter bonds show some variation of length (1·370–1·442 Å), but the pattern of 'longer' and 'shorter' bonds does not correspond to any molecules such as azulene, pentalene and/or heptafulvene, of which the present ring skeleton is formally composed. Excluding the two longest bonds, C(1)—C(14) 1·439 Å and C(13)—C(14) 1·442 Å, which are associated with the electronegative methoxycarbonyl group, the variation (1·370–1·428 Å) is much reduced. Furthermore, it should be mentioned that the variation and also the pattern are quite similar to those in *syn*-bridged [14]annulenes with aromatic perimeters, the structures of which have been studied by Destro, Pilati & Simonetta (1980, and references therein). In contrast to the perimeter bonds, the central C(15)—C(16) bond is 1·347 Å, showing double-bond character. Thus, the pattern of the observed bond lengths, which can be described by the chemical formula (1*A*), conforms to the prediction of a 14π peripheral aromatic system.



(1*A*)

Table 1. *Atomic parameters*

Positional parameters are multiplied by 10^4 for the non-hydrogen atoms and by 10^3 for the hydrogen atoms. Thermal parameters are given by the equivalent temperature factors defined by $B_{\rm eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{\rm eq}$ (Å^2)
C(1)	4090 (2)	6691 (2)	10480 (2)	3·0
C(2)	4547 (2)	7474 (2)	11440 (3)	4·0
C(3)	5393 (2)	8199 (2)	11410 (3)	4·5
C(4)	6027 (3)	8380 (2)	10516 (3)	4·6
C(5)	6020 (2)	7891 (2)	9363 (3)	3·9
C(6)	5291 (2)	7038 (2)	8773 (2)	3·2
C(7)	5187 (2)	6456 (2)	7603 (2)	3·3
C(8)	4315 (2)	5658 (2)	7479 (2)	3·5
C(9)	3901 (2)	4879 (2)	6523 (3)	4·4
C(10)	3060 (3)	4148 (2)	6529 (3)	4·9
C(11)	2437 (2)	3943 (2)	7424 (3)	4·7
C(12)	2434 (2)	4412 (2)	8597 (3)	4·0
C(13)	3113 (2)	5292 (2)	9180 (3)	3·3
C(14)	3228 (2)	5878 (2)	10377 (2)	3·1
C(15)	4466 (2)	6582 (2)	9350 (2)	3·1
C(16)	3898 (2)	5772 (2)	8594 (2)	3·1
C(17)	5837 (3)	6682 (2)	6643 (3)	4·4
C(18)	5058 (3)	7367 (2)	5457 (3)	5·9
C(19)	2650 (2)	5714 (2)	11361 (3)	3·8
C(20)	1128 (3)	4755 (2)	11876 (3)	5·7
O(1)	2885 (2)	6170 (2)	12423 (2)	5·4
O(2)	1773 (2)	4968 (1)	10963 (2)	4·6
H(2)	424 (2)	750 (2)	1211 (2)	4·2
H(3)	560 (2)	870 (2)	1205 (2)	5·2
H(4)	658 (2)	895 (2)	1077 (2)	5·8
H(5)	652 (2)	818 (1)	891 (2)	3·5
H(9)	419 (2)	481 (2)	582 (2)	5·3
H(10)	285 (2)	368 (2)	584 (2)	4·7
H(11)	190 (2)	334 (2)	722 (2)	6·0
H(12)	198 (2)	415 (2)	903 (2)	4·4
H(171)	671 (2)	697 (2)	724 (2)	5·4
H(172)	600 (2)	607 (2)	631 (2)	7·3
H(181)	556 (2)	750 (2)	499 (3)	5·2
H(182)	494 (3)	806 (2)	593 (3)	6·0
H(183)	428 (3)	703 (2)	489 (3)	7·5
H(201)	32 (3)	461 (3)	1136 (4)	7·3
H(202)	165 (3)	435 (3)	1251 (4)	8·2
H(203)	106 (3)	531 (3)	1229 (4)	6·0

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38607 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Further evidence for peripheral aromaticity is a coplanar conformation throughout the ring skeleton. The maximum deviation of the 16 C atoms from the ring plane is only 0·029 Å and, as a result, all internal bond angles are distorted to some extent from the sp^2 angle; the greatest strain is imposed on the central C(15) and C(16) atoms, with angles of 110, 110 and 140°.

The crystal structure viewed along the *c* axis is shown in Fig. 2. The two molecules related by a center of symmetry are in close contact, with an interplanar distance of 3·40 Å. The stacking feature is shown in Fig. 3. Closer contacts of atoms are found between the C(14)–C(13)–C(12) and C(6)–C(15)–C(16)–C(8) bonds. The former is adjacent to the methoxycarbonyl group and the latter involves the electron-rich double bond. Although the observed distances of 3·46–3·56 Å are almost at the shortest limits of the van der Waals distances for contacts of this type (Pauling, 1960), the electrostatic interaction may also contribute to the total energy in the crystalline state.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

E.s.d.'s are in parentheses.

C(1)–C(2)	1·403 (3)	1·406*	C(2)C(1)C(14)	131·8 (2)
C(2)–C(3)	1·375 (4)	1·378	C(2)C(1)C(15)	121·8 (2)
C(3)–C(4)	1·413 (4)	1·416	C(14)C(1)C(15)	106·5 (2)
C(4)–C(5)	1·373 (4)	1·376	C(1)C(2)C(3)	125·0 (2)
C(5)–C(6)	1·401 (3)	1·405	C(2)C(3)C(4)	133·1 (2)
C(6)–C(7)	1·418 (3)	1·422	C(3)C(4)C(5)	132·6 (2)
C(7)–C(8)	1·428 (3)	1·431	C(4)C(5)C(6)	125·0 (2)
C(8)–C(9)	1·392 (3)	1·396	C(5)C(6)C(7)	131·3 (2)
C(9)–C(10)	1·370 (4)	1·373	C(5)C(6)C(15)	121·9 (2)
C(10)–C(11)	1·411 (4)	1·413	C(7)C(6)C(15)	106·8 (2)
C(11)–C(12)	1·383 (4)	1·386	C(6)C(7)C(8)	107·8 (2)
C(12)–C(13)	1·408 (3)	1·412	C(6)C(7)C(17)	125·3 (2)
C(13)–C(14)	1·442 (3)	1·445	C(8)C(7)C(17)	126·9 (2)
C(1)–C(14)	1·439 (3)	1·442	C(7)C(8)C(9)	130·5 (2)
C(15)–C(16)	1·347 (3)	1·350	C(7)C(8)C(16)	106·8 (2)
C(1)–C(15)	1·420 (3)	1·423	C(9)C(8)C(16)	122·8 (2)
C(13)–C(16)	1·425 (4)	1·428	C(8)C(9)C(10)	124·6 (2)
C(8)–C(16)	1·435 (4)	1·438	C(9)C(10)C(11)	132·8 (2)
C(6)–C(15)	1·439 (3)	1·441	C(10)C(11)C(12)	133·2 (2)
C(7)–C(17)	1·449 (4)	1·503	C(11)C(12)C(13)	124·8 (2)
C(17)–C(18)	1·512 (3)	1·516	C(12)C(13)C(14)	132·7 (3)
C(14)–C(19)	1·445 (4)	1·447	C(16)C(13)C(12)	121·3 (2)
C(19)–O(1)	1·203 (3)	1·206	C(16)C(13)C(14)	106·0 (2)
C(19)–O(2)	1·353 (3)	1·356	C(1)C(14)C(13)	107·4 (2)
O(2)–C(20)	1·448 (4)	1·451	C(1)C(14)C(19)	123·5 (2)
			C(13)C(14)C(19)	129·1 (2)
			C(1)C(15)C(6)	140·6 (2)
			C(1)C(15)C(16)	109·9 (2)
			C(6)C(15)C(16)	109·5 (2)
			C(13)C(16)C(8)	140·5 (2)
			C(13)C(16)C(15)	110·2 (2)
			C(8)C(16)C(15)	109·3 (2)
			C(7)C(17)C(18)	113·1 (2)
C(sp^2)–H	0·90–1·10		O(1)C(19)O(2)	121·5 (2)
C(sp^3)–H	1·00–1·20		C(19)O(2)C(20)	116·5 (2)

* Corrected for thermal motion.

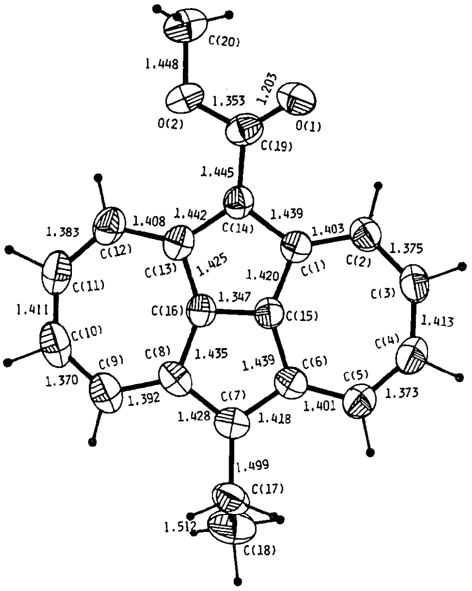

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound. Thermal ellipsoids are drawn at the 50% probability level and on an arbitary scale for H atoms. Uncorrected bond lengths for the non-hydrogen atoms are shown in Å.

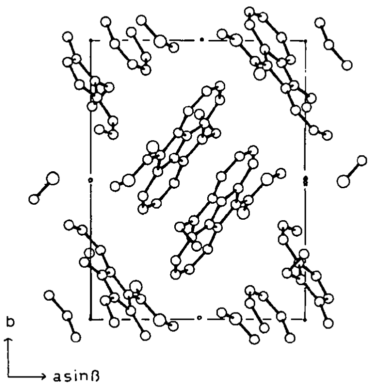

Fig. 2. Crystal structure viewed along the *c* axis. H atoms are omitted for clarity.

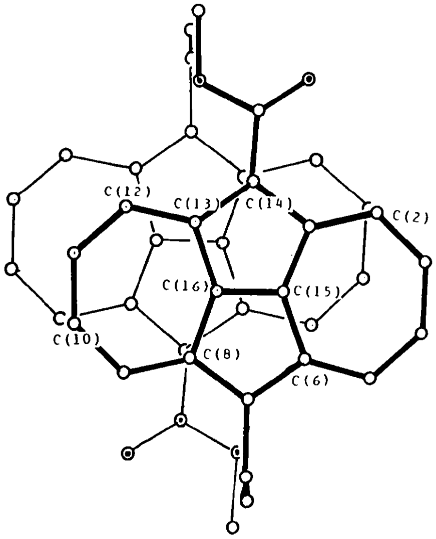

Fig. 3. Stacking diagram of a pair of molecules approaching each other as viewed normal to the least-squares plane of the ring skeleton. Short distances less than 3·65 Å are: C(14)···C(8) = 3·47, C(2)···C(10) = 3·46, C(13)···C(16) = 3·55, C(12)···C(6) = 3·51, C(12)···C(15) = 3·55 Å.

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Structures of Two N-Bridgehead C-Nucleosides: 5,7-Dimethyl-3-β-D-ribofuranosyl[1,2,4]triazolo[4,3-*a*]pyrimidine, $C_{12}H_{16}N_4O_4$ (I), and 5,7-Dimethyl-2-β-D-ribofuranosyl[1,2,4]triazolo[1,5-*a*]pyrimidine–Methanol, $C_{12}H_{16}N_4O_4.CH_4O$ (II)

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Abstract. (I): $M_r = 280{\cdot}29$, monoclinic, $C2$, $a = 22{\cdot}152\,(6)$, $b = 7{\cdot}225\,(2)$, $c = 25{\cdot}530\,(5)$ Å, $\beta = 103{\cdot}7\,(2)^\circ$, $Z = 12$, $U = 3969{\cdot}02$ Å^3, $D_x = 1{\cdot}412$ Mg m^{-3}, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}920$ mm^{-1}, $F(000) = 1776$, room temperature. (II): $M_r = 312{\cdot}33$, orthorhombic, $P2_12_12_1$, $a = 23{\cdot}318\,(9)$, $b = 10{\cdot}109\,(4)$, $c = 6{\cdot}858\,(2)$ Å, $Z = 4$, $U = 1616{\cdot}58$ Å^3, $D_x = 1{\cdot}287$ Mg m^{-3}, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}852$ mm^{-1}, $F(000) = 664$, room temperature. Final $R = 0{\cdot}075$ for 3157 observed reflexions (I) and $R = 0{\cdot}064$ for 1352 observed reflexions (II) $[I > 2\sigma(I)]$. There are three asymmetric units (*A*, *B*, *C*) in the structure of (I) with different ribose puckers: an envelope $_2E$, $P = 340{\cdot}4^\circ$ (*A*), twisted $^2T_1$, $P = 145{\cdot}7^\circ$ (*B*) and $^3T_4$, $P = 27{\cdot}7^\circ$ (*C*). In (II) the ribose appears in a twisted $^2T_3$, $P = 181{\cdot}7^\circ$, conformation. Sugar conformations around C(4')–C(5') in (I) are *trans*, $\psi = 177{\cdot}6^\circ$ (*A*), *gauche*$^+$, $\psi = 56{\cdot}3^\circ$ (*B*), $\psi = 38{\cdot}0^\circ$ (*C*), and in (II) *trans*, $\psi = -177{\cdot}6^\circ$. The conformation about the C-glycosyl bond is high-*anti* [$\chi = 109{\cdot}6$ (*A*), $117{\cdot}0$ (*B*) and $107{\cdot}2^\circ$ (*C*)] in (I) and *anti* ($\chi = 72{\cdot}0^\circ$) in (II). The molecular packing is dominated by hydrogen bonds. A three-dimensional system of hydrogen bonds is formed by sugar–sugar interactions [O(2')–H···O(3'), 2·892 (7), *A*···*C*; O(3')–H···O(5'), 2·814 (7), *B*···*A*; O(5')–H···O(2'), 2·861 (9) Å, *B*···*B*] and sugar–base [O(3')–H···N(2), 2·942 (8), *A*···*C*; O(5')–H···N(1), 2·837 (7), *A*···*B*; 2·871 (11), *C*···*A*; O(2')–H···N(2), 2·842 (8), *B*···*B*; O(2')–H···N(1), 2·817 (10), *C*···*C*; O(3')–H···N(8), 2·868 (9) Å, *C*···*A*] in (I). In (II) there are sugar–sugar [O(2')–H···O(5'), 2·720 (7); O(5')–H···O(3'), 2·695 (7) Å], sugar–solvent [O(3')–H···O(1), 2·731 (8) Å], and solvent–base [O(1)–H···N(1), 2·858 (7) Å] interactions. Base stacking does not occur in these structures.

Introduction. Our interest within the series of N-bridgehead nucleosides (Kojić-Prodić, Ružić-Toroš, Golič, Brdar & Kobe, 1982) is further extended to 3-β-D-ribofuranosyl[1,2,4]triazolo[4,3-*a*]pyrimidine (I) and 2-β-D-ribofuranosyl[1,2,4]triazolo[1,5-*a*]pyrimidine (II), basic heterocyclic systems considered as potential analogues of the antibiotics formycin A and B (Brdar, Japelj & Kobe, 1979).

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