

Research partly supported by DK 41009 and American Heart Association, New York State Affiliate 87-095G.

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*Acta Cryst.* (1991). **C47**, 790–793

## Structure of a New Dammarane-type Triterpene\* from *Gynostemma pentaphyllum* (Thurb.) Makino

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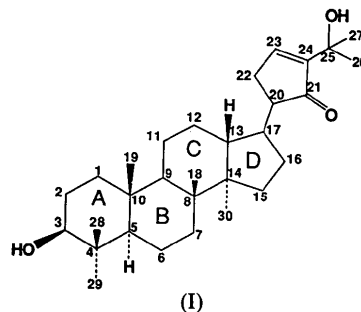
(Received 8 May 1990; accepted 11 July 1990)

**Abstract.**  $C_{30}H_{48}O_3$ ,  $M_r = 456.7$ , monoclinic,  $C2$ ,  $a = 35.515$  (2),  $b = 6.758$  (1),  $c = 11.116$  (1) Å,  $\beta = 97.59$  (1)°,  $V = 2644.6$  (8) Å<sup>3</sup>,  $D_m(\text{floatation}) = 1.153$  (5),  $D_x = 1.147$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 1008$ ,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 0.48$  mm<sup>-1</sup>,  $T = 290$  (1) K. Final  $R = 0.042$  for 2346 observed data. The molecular structure is based on a tetracyclic triterpenoid skeleton of the dammarane type and is a diol with the dammarane side chain modified to a cyclopentenone moiety. Intermolecular hydrogen bonds involving both hydroxyl groups link the molecules into double layers parallel to the  $ab$  plane in the crystal.

**Introduction.** *Gynostemma pentaphyllum* (Thurb.) Makino (family Cucurbitaceae) is a perennial creeping herb widely distributed in China, Japan, Korea and southeast Asia. It was used as a sweetener in Japan and has been used as a folk medicine in China for relieving inflammation and coughs, as an expectorant and for treating chronic bronchitis and infectious hepatitis (Zhou, 1988). Studies on its chemical constituents were begun by Nagai, Nagumo & Izawa (1976) and now more than 80 dammarane-type saponins (gynpenosides) have been isolated and identified. Several of these were identified as ginsen-

osides previously isolated from *Panax ginseng* C. A. Meyer (Ollis & Shibata, 1986), a well known traditional Chinese medicine. Because of their biological activities, much attention is now focused on gynpenosides.

Acid hydrolysis of a glycoside mixture from *Gynostemma pentaphyllum* (Thurb.) Makino from Yunnan China locations yielded three aglycones, one of these being the gynogenin reported here. Subsequent <sup>13</sup>C NMR and mass-spectral data indicated that the latter has a molecular structure based on a tetracyclic triterpenoid skeleton of dammarane type, but the NMR data showed it to differ from other known dammarane-type sapogenins. An X-ray analysis has now defined the molecular structure of this hitherto unknown gynogenin as (I).



\* (20R)-3 $\beta$ ,25-Dihydroxy-21,24-cyclo-dammar-23-en-21-one.

**Experimental.** Colorless plate-like crystals from a petroleum ether/acetone mixture (m.p. 509–510 K); a crystal  $ca\ 0.10 \times 0.51 \times 0.66$  mm aligned on a Rigaku-AFC diffractometer; cell parameters determined by least squares for 25 strong reflections ( $45 < 2\theta < 80^\circ$ ); Cu  $K\alpha$  radiation (graphite-crystal monochromator);  $\omega$ - $2\theta$  scan,  $2\theta$  scan rate  $2^\circ\ \text{min}^{-1}$ , scan range ( $\Delta\omega$ )  $(1.2 + 0.5\tan\theta)^\circ$ ,  $2\theta_{\text{max}} = 130^\circ$ , 10 s stationary background counts; three standard reflections, no significant intensity variations; 2450 non-equivalent terms ( $h - 41$  to  $41$ ,  $k 0$  to  $7$ ,  $l 0$  to  $13$ ), 2346 with  $I \geq 1.0\sigma(I)$  were used for structure refinement; intensities corrected for Lorentz and polarization effects and for absorption (transmission factors 0.925 to 0.772).

Structure solved by direct methods with *SHELXS86* (Sheldrick, 1985). Hydroxyl H atoms omitted; H atoms bonded to C atoms included at idealized positions (C—H 1.08 Å). Full-matrix refinement with *SHELX76* (Sheldrick, 1976) with anisotropic temperature factors given to the C and O atoms, common isotropic for methyl H atoms and individual isotropic for non-methyl H atoms converged at  $R = 0.042$ ,  $wR = 0.062$ ,  $S = 2.32$  (323 parameters varied); function minimized  $\sum w(\Delta F)^2$  with  $w = (\delta|F_o|^2 + 0.0005|F_o|^2)^{-1}$ ;  $(\Delta/\sigma)_{\text{max}} = 0.01$ ,  $(\Delta\rho)_{\text{max}}$ ,  $(\Delta\rho)_{\text{min}} = +0.15$ ,  $-0.14\ \text{e}\ \text{Å}^{-3}$ . Three intense low-order terms (111,  $\bar{1}11$ , 002) apparently seriously affected by extinction omitted from final refinement. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149). Figures were prepared from the output of *ORTEPII* (Johnson, 1976). Calculations performed on a VAX8800 computer.

**Discussion.** Final atomic coordinates are given in Table 1.\* The molecular conformation and numbering scheme are illustrated in Fig. 1, bond lengths, valence angles and selected torsion angles are listed in Table 2.

A perspective view of the molecule is shown in Fig. 1. It has a molecular skeleton based on that of dammarane but is a  $3\beta,25$ -diol with the  $17\beta$  side chain of dammarane modified to a 21,24-cyclopent-23-en-21-one moiety. The absolute configuration follows from the known configuration of other dammarane triterpenes, with the configuration at C(20) established as *R*. The tetracyclic ring system adopts a conformation similar to that observed in several dammarane sapogenins isolated from *Panax notogin-*

Table 1. Final atomic coordinates and equivalent isotropic temperature factors ( $\text{Å}^2$ ) for the non-H atoms with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = 8\pi^2 U_{\text{eq}} = 8\pi^2/3 \sum_j U_{ij} a_j^* a_j^* a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$
C(1)	3922 (1)	8632	5574 (2)	4.0 (1)
C(2)	4347 (1)	8644 (8)	5483 (2)	4.5 (1)
C(3)	4556 (1)	10030 (8)	6417 (2)	4.1 (1)
C(4)	4504 (1)	9527 (8)	7743 (2)	3.6 (1)
C(5)	4066 (1)	9374 (6)	7785 (2)	2.8 (1)
C(6)	3958 (1)	9040 (8)	9060 (2)	3.8 (1)
C(7)	3542 (1)	9645 (8)	9082 (2)	3.7 (1)
C(8)	3264 (1)	8458 (6)	8185 (2)	2.8 (1)
C(9)	3402 (1)	8494 (6)	6897 (2)	2.6 (1)
C(10)	3829 (1)	7993 (6)	6840 (2)	3.0 (1)
C(11)	3123 (1)	7355 (8)	5956 (2)	3.6 (1)
C(12)	2722 (1)	8254 (8)	5843 (2)	3.7 (1)
C(13)	2585 (1)	8263 (6)	7082 (2)	2.9 (1)
C(14)	2856 (1)	9408 (6)	8033 (2)	2.9 (1)
C(15)	2633 (1)	9261 (8)	9126 (2)	4.1 (1)
C(16)	2213 (1)	9515 (8)	8581 (2)	4.1 (1)
C(17)	2195 (1)	9126 (6)	7202 (2)	3.3 (1)
C(18)	3247 (1)	6348 (8)	8685 (3)	4.5 (2)
C(19)	3917 (1)	5762 (8)	7014 (4)	5.0 (2)
C(20)	1845 (1)	7907 (8)	6677 (2)	3.5 (2)
C(21)	1483 (1)	8948 (6)	6929 (2)	3.4 (2)
C(22)	1803 (1)	5799 (6)	7149 (3)	4.1 (2)
C(23)	1400 (1)	5701 (8)	7409 (3)	3.8 (1)
C(24)	1222 (1)	7449 (8)	7311 (2)	3.3 (1)
C(25)	825 (1)	7907 (8)	7571 (3)	3.9 (1)
C(26)	594 (1)	8918 (9)	6500 (3)	5.3 (1)
C(27)	845 (1)	9221 (10)	8696 (3)	6.2 (1)
C(28)	4730 (1)	7658 (9)	8198 (3)	5.3 (1)
C(29)	4658 (1)	11278 (9)	8534 (3)	4.8 (2)
C(30)	2866 (1)	11631 (8)	7701 (3)	4.3 (2)
O(3)	4953 (1)	10021 (8)	6255 (2)	6.2 (1)
O(21)	1429 (1)	10721 (6)	6850 (2)	5.1 (1)
O(25)	640 (1)	6091 (6)	7821 (2)	5.5 (1)

*seng* (Burk.) F. H. Chen (Wei *et al.*, 1982, 1984; Puff, Friedrichs, Habscheid, Quante & Chen, 1986) and a dammarane triterpene from *Betula costata* Trautv. (Iljin, Malinovskaya, Uvarova, Elyakou, Antipin & Struchkov, 1982). Rings *A*, *B* and *C* have chair forms. The conformational asymmetry parameters (Duax & Norton, 1975) for these rings are  $\Delta C_s^2$  1.2,  $\Delta C_2^{3,4}$  5.8° (ring *A*),  $\Delta C_s^{5,6}$  1.7,  $\Delta C_2^7$  11.3° (ring *B*) and  $\Delta C_s^8$  0.5,  $\Delta C_2^{9,11}$  1.0° (ring *C*). Ring *D* adopts a  $13\beta,14\alpha$  half-chair conformation with C(13) and C(14) lying on opposite sides of the C(15), C(16), C(17) plane at respective distances of 0.290 (5) and 0.453 (5) Å. The pseudorotation parameters (Altona, Geise & Romers, 1968) for the *D* ring are  $\Delta = -7.3^\circ$  and  $\varphi_m = 47^\circ$ . The intramolecular spacing C(3)⋯C(16) of 8.97 (1) Å, a measure used for comparing the overall length of the tetracyclic system, lies within the range of values 8.86 to 9.01 Å observed in comparable molecules (Park & Craven, 1981). The  $17\beta$ -cyclopentenone attachment [ring atoms coplanar to within  $\pm 0.063$  (5) Å] is edge on to the tetracyclic nucleus and the torsion angle C(13)—C(17)—C(20)—C(21) of 177.4 (3)° defines its orientation relative to the *D* ring.

The bond lengths and angles are in good agreement with those reported for comparable structures. The C( $sp^3$ )—C( $sp^3$ ) bond lengths range from 1.516 (5) to 1.574 (4) Å and the endocyclic angles in

\* Lists of structure amplitudes, anisotropic temperature factors, H-atom coordinates and intermolecular contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53405 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Molecular geometry* (Å, °) for C<sub>30</sub>H<sub>48</sub>O<sub>3</sub> with *e.s.d.'s in parentheses*

E.s.d.'s for torsion angles are ca 0.4°.

C(1)—C(2)	1.526 (5)	C(12)—C(13)	1.520 (4)
C(1)—C(10)	1.548 (4)	C(13)—C(14)	1.541 (5)
C(2)—C(3)	1.517 (5)	C(13)—C(17)	1.525 (5)
C(3)—C(4)	1.547 (4)	C(14)—C(15)	1.539 (4)
C(3)—O(3)	1.445 (5)	C(14)—C(30)	1.548 (7)
C(4)—C(5)	1.562 (5)	C(15)—C(16)	1.544 (5)
C(4)—C(28)	1.545 (7)	C(16)—C(17)	1.548 (3)
C(4)—C(29)	1.531 (7)	C(17)—C(20)	1.540 (5)
C(5)—C(6)	1.534 (4)	C(20)—C(21)	1.523 (6)
C(5)—C(10)	1.564 (5)	C(20)—C(22)	1.533 (7)
C(6)—C(7)	1.536 (5)	C(21)—C(24)	1.473 (6)
C(7)—C(8)	1.534 (5)	C(21)—O(21)	1.215 (7)
C(8)—C(9)	1.574 (4)	C(22)—C(23)	1.499 (5)
C(8)—C(14)	1.573 (5)	C(23)—C(24)	1.337 (7)
C(8)—C(18)	1.535 (7)	C(24)—C(25)	1.508 (5)
C(9)—C(10)	1.566 (5)	C(25)—C(26)	1.516 (5)
C(9)—C(11)	1.547 (5)	C(25)—C(27)	1.527 (7)
C(10)—C(19)	1.547 (7)	C(25)—O(25)	1.437 (6)
C(11)—C(12)	1.538 (6)		
C(2)—C(1)—C(10)	113.0 (3)	C(11)—C(12)—C(13)	109.3 (3)
C(1)—C(2)—C(3)	110.9 (3)	C(12)—C(13)—C(14)	112.2 (3)
C(2)—C(3)—C(4)	114.0 (3)	C(12)—C(13)—C(17)	118.9 (3)
C(2)—C(3)—O(3)	108.0 (3)	C(14)—C(13)—C(17)	103.9 (3)
C(4)—C(3)—O(3)	111.0 (3)	C(8)—C(14)—C(13)	110.6 (3)
C(3)—C(4)—C(5)	106.7 (3)	C(8)—C(14)—C(15)	116.8 (3)
C(3)—C(4)—C(28)	111.7 (3)	C(8)—C(14)—C(30)	111.8 (3)
C(3)—C(4)—C(29)	107.4 (3)	C(13)—C(14)—C(15)	99.7 (3)
C(5)—C(4)—C(28)	114.3 (3)	C(13)—C(14)—C(30)	110.8 (3)
C(5)—C(4)—C(29)	108.4 (3)	C(15)—C(14)—C(30)	106.3 (3)
C(28)—C(4)—C(29)	108.2 (3)	C(14)—C(15)—C(16)	104.7 (3)
C(4)—C(5)—C(6)	114.2 (3)	C(15)—C(16)—C(17)	106.3 (3)
C(4)—C(5)—C(10)	117.9 (3)	C(13)—C(17)—C(16)	103.4 (3)
C(6)—C(5)—C(10)	110.7 (3)	C(13)—C(17)—C(20)	117.4 (3)
C(5)—C(6)—C(7)	109.6 (3)	C(16)—C(17)—C(20)	113.1 (3)
C(6)—C(7)—C(8)	112.8 (3)	C(17)—C(20)—C(21)	110.0 (3)
C(7)—C(8)—C(9)	109.4 (3)	C(17)—C(20)—C(22)	118.5 (3)
C(7)—C(8)—C(14)	111.2 (3)	C(21)—C(20)—C(22)	104.1 (3)
C(7)—C(8)—C(18)	107.7 (3)	C(20)—C(21)—C(24)	108.3 (3)
C(9)—C(8)—C(14)	106.8 (3)	C(20)—C(21)—O(21)	124.8 (3)
C(9)—C(8)—C(18)	112.1 (3)	C(24)—C(21)—O(21)	126.9 (3)
C(14)—C(8)—C(18)	109.8 (3)	C(20)—C(22)—C(23)	104.2 (3)
C(8)—C(9)—C(10)	117.0 (3)	C(22)—C(23)—C(24)	113.5 (3)
C(8)—C(9)—C(11)	111.0 (3)	C(21)—C(24)—C(23)	108.8 (3)
C(10)—C(9)—C(11)	113.8 (3)	C(21)—C(24)—C(25)	123.6 (3)
C(1)—C(10)—C(5)	106.5 (3)	C(23)—C(24)—C(25)	127.6 (3)
C(1)—C(10)—C(9)	107.4 (3)	C(14)—C(25)—C(26)	111.4 (3)
C(1)—C(10)—C(19)	108.8 (3)	C(24)—C(25)—C(27)	109.4 (3)
C(5)—C(10)—C(9)	106.5 (3)	C(24)—C(25)—O(25)	108.9 (3)
C(5)—C(10)—C(19)	114.7 (3)	C(26)—C(25)—C(27)	110.1 (3)
C(9)—C(10)—C(19)	112.6 (3)	C(26)—C(25)—O(25)	108.8 (3)
C(9)—C(11)—C(12)	111.2 (3)	C(27)—C(25)—O(25)	108.1 (3)
C(1)—C(2)—C(3)—C(4)	57.9	C(13)—C(14)—C(15)—C(16)	-39.1
C(2)—C(3)—C(4)—C(5)	-52.3	C(14)—C(15)—C(16)—C(17)	17.7
C(3)—C(4)—C(5)—C(10)	52.0	C(13)—C(17)—C(16)—C(15)	11.3
C(1)—C(10)—C(5)—C(4)	-53.1	C(14)—C(13)—C(17)—C(16)	-36.3
C(2)—C(1)—C(10)—C(5)	53.9	C(15)—C(14)—C(13)—C(17)	46.9
C(3)—C(2)—C(1)—C(10)	-58.7	C(1)—C(2)—C(3)—O(3)	-178.1
C(5)—C(6)—C(7)—C(8)	59.9	C(4)—C(5)—C(10)—C(19)	67.3
C(6)—C(7)—C(8)—C(9)	-50.3	C(6)—C(7)—C(8)—C(18)	71.7
C(7)—C(8)—C(9)—C(10)	48.5	C(7)—C(8)—C(14)—C(30)	53.1
C(5)—C(10)—C(9)—C(8)	-52.1	C(16)—C(17)—C(20)—C(22)	-62.4
C(6)—C(5)—C(10)—C(9)	58.4	C(17)—C(20)—C(21)—O(21)	40.9
C(7)—C(6)—C(5)—C(10)	-64.3	C(20)—C(21)—C(24)—C(23)	5.1
C(8)—C(9)—C(11)—C(12)	59.2	C(21)—C(24)—C(23)—C(22)	1.8
C(9)—C(11)—C(12)—C(13)	-56.8	C(20)—C(22)—C(23)—C(24)	-7.9
C(11)—C(12)—C(13)—C(14)	57.4	C(21)—C(20)—C(22)—C(23)	10.1
C(8)—C(14)—C(13)—C(12)	-59.7	C(22)—C(20)—C(21)—C(24)	-9.6
C(9)—C(8)—C(14)—C(13)	57.9	C(25)—C(24)—C(21)—O(21)	5.2
C(11)—C(9)—C(8)—C(14)	-58.1		

because of the severe strain caused by the fusion of the five- and six-membered rings.

The crystal packing (Fig. 2) can be described in terms of the notation for steroid crystals (Bernal, Crowfoot & Fankuchen, 1940), *viz* 122. The molecules are aligned with their long axes along the [100] direction and are linked head-to-head into dimers by intermolecular hydrogen bonds involving the A-ring

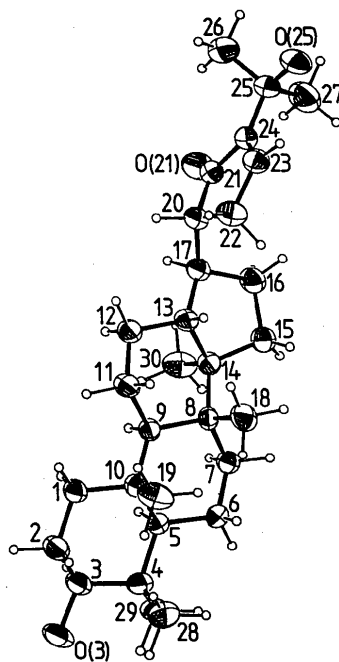


Fig. 1. A perspective view of the molecule with thermal ellipsoids scaled to 50% probability. The symbol C is omitted for carbon and the H atoms are denoted by spheres of arbitrary radius.

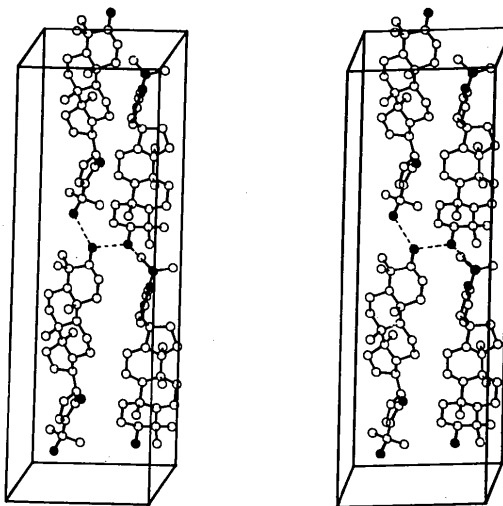


Fig. 2. Stereoview of the crystal packing. Direction of projection *b* and the *a* axis is vertical.

rings *A*, *B* and *C* range between 106.5 (3) and 113.0 (2)°. The angle C(13)—C(14)—C(15) of 99.7 (3)° in ring *D*, and the two exocyclic angles C(12)—C(13)—C(17) and C(8)—C(14)—C(15) of 118.9 (3) and 116.8 (3)°, respectively, reflect the usual distortions from the regular tetrahedral value

hydroxyl groups of adjacent molecules related by a twofold axis; the O(3)···O(3) ( $1-x, y, 1-z$ ) spacing is 2.853 (3) Å. Although the hydroxyl H-atom site was not located, it can be presumed that the oxygen acts both as a donor and an acceptor in this interaction which results in a four-atom dimer ring containing two oxygens and their protons. The dimers are linked by hydrogen bonds between the C(25) hydroxyl substituent and O(3) into double layers parallel to the *ab* crystal plane; the O(25)···O(3) ( $-\frac{1}{2}+x, -\frac{1}{2}+y, z$ ) spacing is 2.896 (5) Å. These layers are held together in the crystal by van der Waals interactions. All other intermolecular contacts are normal.

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*Acta Cryst.* (1991). **C47**, 793–797

## Crystal Structure and Photochemistry of a Methyl Phenyl Diester Derivative of Dibenzobarrelene\*

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(Received 9 February 1990; accepted 13 July 1990)

**Abstract.** Methyl phenyl dibenzobarrelene-2,3-dicarboxylate,  $C_{25}H_{18}O_4$ ,  $M_r = 382.42$ , monoclinic,  $P2_1/c$ ,  $a = 11.557$  (1),  $b = 9.170$  (1),  $c = 18.714$  (1) Å,  $\beta = 93.20$  (1)°,  $V = 1980$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.282$  g cm<sup>-3</sup>,  $Cu K\alpha_1$ ,  $\lambda = 1.54056$  Å,  $\mu = 6.64$  cm<sup>-1</sup>,  $F(000) = 800$ ,  $T = 295$  K,  $R = 0.046$  for 2535 reflections with  $I \geq 3\sigma(I)$ . The two ester carbonyl groups show different degrees of conjugation to the central double bond, with the relevant bond lengths indicating some extent of electron delocalization over the  $\alpha,\beta$ -unsaturated carbonyl system. The length of the bridging double bond [C11=C12, 1.336 (3) Å] is virtually the same as in the methyl isopropyl diester [1.334 (4) Å] and in agreement with that of the dicarbonitrile [1.343 (5) Å] derivatives of dibenzobarrelene. The aromatic ring of the phenoxy-

carbonyl group is rotated 60° out of its carbonyl plane; the O—C(Ph) bond in the phenyl ester [1.407 (3) Å] is significantly shorter than the corresponding O—C(Me) [1.443 (3) Å]. Two regioisomeric photoproducts are obtained upon photolysis, with identical product ratios in the solid state and in solution. Analysis of the photochemical pathways from crystal-structure and molecular-conformational points of view leads to the same predicted major product, which is consistent with the experimental results.

**Introduction.** Crystal and photochemical studies (Scheffer, Trotter, Garcia-Garibay & Wireko, 1988; Garcia-Garibay, Scheffer, Trotter & Wireko, 1990*a,b*) of dibenzobarrelene derivatives have given detailed structural information on the pathways of the di- $\pi$ -methane rearrangement in the solid state. In the case of dibenzobarrelenes substituted at C11 and

\* Methyl phenyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate.