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# Structure of 9-Annulene Derivatives. 1. 5,13-Diphenyl-8*H*-cyclonona[*b*]naphthalene, $C_{29}H_{22}$

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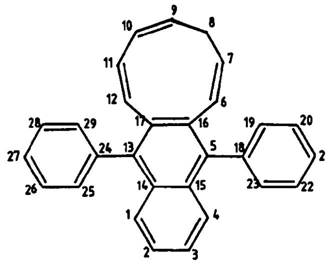
**Abstract.** $M_r = 370\cdot5$, monoclinic, space group $C2/c$, $a = 13\cdot468\ (17)$, $b = 22\cdot137\ (5)$, $c = 13\cdot859\ (2)$ Å, $\beta = 92\cdot22\ (4)°$, $U = 4128\cdot8$ Å$^3$, $Z = 8$, $D_x = 1\cdot19$ Mg m$^{-3}$, $\lambda(\text{Mo }K\alpha) = 0\cdot71073$ Å, $\mu = 0\cdot073$ mm$^{-1}$, $F(000) = 1568$, $T = 295$ K. Final $R = 0\cdot047$ for 2120 observed reflections. The nine-membered ring adopts a distorted tub conformation. There is evidence of steric overcrowding. The molecules are packed by van der Waals interactions.

**Introduction.** Cyclononatetraene, the parent 9-annulene, is an unstable, non-planar, anti-aromatic molecule which readily undergoes valence isomerization to *cis*-8,9-dihydroindene at temperatures above 200 K (Anastassiou, Orfanos & Gebrian, 1969; Baldwin, 1972). Several subsequent investigations have demonstrated that benzene or naphthalene annelation of cyclononatetraene inhibits the isomerization reaction to the extent that solid derivatives stable at room temperature have been prepared (Anastassiou, Libsch & Griffith, 1973; Anastassiou, Kasmai & Sabahi, 1979).

Until now, no solid-state structural studies have been published on these benzene- and naphthalene-annelated cyclononatetraenes; indeed, the only 9-annulene derivative to have been previously investigated, 4-(diethylamino)-1,10-ethano-5-methylcyclopentacyclononene (Lindner, Kitschke, Hafner & Ude, 1980, involves a fused tricyclic ring system with stereochemical constraints markedly different from those of the parent annulene.

The present paper reports results obtained by an X-ray study on a representative naphthalene-annelated cyclononatetraene (I).



(I)

**Experimental.** Suitable crystals prepared by isothermal concentration of an ether solution of (I). Crystal dimensions 0·30 × 0·35 × 0·90 mm. Enraf–Nonius CAD-4 diffractometer, take-off angle 5°, graphite-crystal-monochromatized Mo $K\alpha$ radiation. Cell dimensions obtained by least-squares refinement of setting angles of 25 accurately centred large-angle reflections. 3543 independent reflections (to $\theta < 25°$) measured using $\omega$–$2\theta$ scans, background scans being taken on each side of peaks. Range of $hkl$: −15–16, 0–22, 0–16. Intensities of three standard reflections showed no significant variation during data collection. Automatic multisolution routine of *SHELX76* (Sheldrick, 1976) used to generate a series of $E$ maps, one of which correctly located all non-H atomic positions. 2120 reflections considered observed, having $I \geq 3\,\sigma(I)$, only these used in subsequent steps. $R_{\text{int}} = 0\cdot004$. Three cycles of full-matrix least-squares refinement with isotropic temperature factors gave $R = 0\cdot127$, incorporation of anisotropic temperature factors reduced $R$ to 0·093. All H atoms located at this stage from a difference map and further refinement of non-H atoms anisotropically and H atoms isotropically reduced $R$ to 0·047. Weighting scheme based on counting statistics was used, $w = 3\cdot0/[\sigma^2|F_o| + 0\cdot0003F_o^2]$, minimizing $\sum w\Delta F^2$; $R_w = 0\cdot050$, $S = 3\cdot9$, $\Delta/\sigma = 0\cdot12$. Final difference map showed no peaks or depressions larger than $0\cdot27$ e Å$^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

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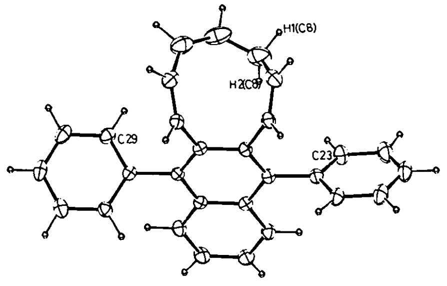

Fig. 1. View of molecule.

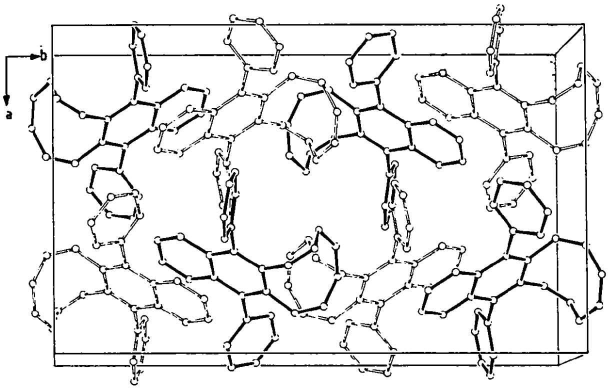

Fig. 2. The molecular packing arrangement. (Bond shading is used to distinguish molecules which overlap along the *c* axis.)

Table 1. *Fractional coordinates* (×10⁴) *and equivalent isotropic U values* (×10³)

$U_{\rm eq} = \frac{1}{3}$(trace of the orthogonalized $U_{ij}$ matrix)

| | *x* | *y* | *z* | $U_{\rm eq}$(Å$^2$) |
|---|---|---|---|---|
| C(1) | 2546 (2) | 2402 (1) | 1399 (2) | 52 |
| C(2) | 1988 (2) | 2917 (1) | 1458 (2) | 61 |
| C(3) | 1382 (2) | 3009 (1) | 2235 (2) | 62 |
| C(4) | 1313 (2) | 2587 (1) | 2936 (2) | 54 |
| C(5) | 1798 (2) | 1587 (1) | 3624 (2) | 46 |
| C(6) | 2272 (2) | 581 (1) | 4298 (2) | 54 |
| C(7) | 1750 (2) | 82 (2) | 4151 (3) | 75 |
| C(8) | 1127 (3) | −31 (3) | 3217 (4) | 113 |
| C(9) | 1585 (4) | −369 (2) | 2461 (4) | 110 |
| C(10) | 2522 (4) | −409 (2) | 2207 (3) | 99 |
| C(11) | 3447 (3) | −133 (1) | 2590 (2) | 71 |
| C(12) | 3668 (2) | 428 (1) | 2813 (2) | 52 |
| C(13) | 3092 (2) | 1406 (1) | 2082 (2) | 42 |
| C(14) | 2511 (2) | 1950 (1) | 2122 (2) | 42 |
| C(15) | 1874 (2) | 2042 (1) | 2902 (2) | 45 |
| C(16) | 2352 (2) | 1062 (1) | 3562 (2) | 45 |
| C(17) | 2998 (2) | 972 (1) | 2788 (2) | 44 |
| C(18) | 1127 (2) | 1660 (1) | 4450 (2) | 51 |
| C(19) | 1525 (3) | 1800 (1) | 5364 (2) | 64 |
| C(20) | 926 (3) | 1826 (2) | 6146 (2) | 79 |
| C(21) | −82 (3) | 1712 (2) | 6029 (3) | 85 |
| C(22) | −499 (3) | 1589 (2) | 5128 (3) | 86 |
| C(23) | 106 (2) | 1566 (2) | 4340 (3) | 71 |
| C(24) | 3797 (2) | 1309 (1) | 1284 (2) | 45 |
| C(25) | 3650 (2) | 833 (1) | 647 (2) | 59 |
| C(26) | 4305 (3) | 734 (2) | −83 (2) | 72 |
| C(27) | 5098 (3) | 1113 (2) | −190 (2) | 75 |
| C(28) | 5259 (3) | 1587 (2) | 433 (2) | 69 |
| C(29) | 4608 (2) | 1685 (1) | 1166 (2) | 53 |

**Discussion.** Fig. 1 is a minimum-overlap view (isometric projection) of the molecule, showing 20% probability vibration ellipsoids for the C atoms and arbitrary spheres of radius 0·05 Å for H atoms. The crystallographic numbering scheme is given in (I), but where ambiguity exists, atom numbers are also given in Fig. 1. Fig. 2 shows the packing arrangement in the crystal. Both figures were produced using *ORTEP* (Johnson, 1976). Table 1 lists the fractional atomic coordinates and Table 2 lists bond distances and angles involving non-H atoms together with the endocyclic torsion angles for the nine-membered ring.*

Table 2. *Molecular geometry*

(*a*) Distances (Å)

| | | | |
|---|---|---|---|
| C(2)—C(1) | 1·369 (4) | C(17)—C(13) | 1·380 (3) |
| C(14)—C(1) | 1·418 (3) | C(24)—C(13) | 1·501 (3) |
| C(3)—C(2) | 1·391 (4) | C(15)—C(14) | 1·420 (3) |
| C(4)—C(3) | 1·355 (4) | C(17)—C(16) | 1·421 (3) |
| C(15)—C(4) | 1·426 (3) | C(19)—C(18) | 1·390 (4) |
| C(15)—C(5) | 1·426 (3) | C(23)—C(18) | 1·393 (4) |
| C(16)—C(5) | 1·385 (3) | C(20)—C(19) | 1·378 (4) |
| C(18)—C(5) | 1·495 (3) | C(21)—C(20) | 1·384 (5) |
| C(7)—C(6) | 1·322 (4) | C(22)—C(21) | 1·376 (5) |
| C(16)—C(6) | 1·481 (3) | C(23)—C(22) | 1·389 (5) |
| C(8)—C(7) | 1·535 (6) | C(25)—C(24) | 1·385 (3) |
| C(9)—C(8) | 1·445 (6) | C(29)—C(24) | 1·389 (3) |
| C(10)—C(9) | 1·327 (6) | C(26)—C(25) | 1·384 (4) |
| C(11)—C(10) | 1·468 (5) | C(27)—C(26) | 1·370 (5) |
| C(12)—C(11) | 1·312 (4) | C(28)—C(27) | 1·371 (5) |
| C(17)—C(12) | 1·504 (3) | C(29)—C(28) | 1·384 (4) |
| C(14)—C(13) | 1·439 (3) | | |

(*b*) Angles (°)

| | | | |
|---|---|---|---|
| C(14)—C(1)—C(2) | 120·8 (3) | C(6)—C(16)—C(5) | 120·4 (2) |
| C(3)—C(2)—C(1) | 120·5 (3) | C(17)—C(16)—C(5) | 120·8 (2) |
| C(4)—C(3)—C(2) | 120·8 (3) | C(17)—C(16)—C(6) | 118·8 (2) |
| C(15)—C(4)—C(3) | 120·6 (3) | C(13)—C(17)—C(12) | 120·2 (2) |
| C(16)—C(5)—C(15) | 119·7 (2) | C(16)—C(17)—C(12) | 118·6 (2) |
| C(18)—C(5)—C(15) | 121·5 (2) | C(16)—C(17)—C(13) | 120·8 (2) |
| C(18)—C(5)—C(16) | 118·8 (2) | C(19)—C(18)—C(5) | 119·9 (2) |
| C(16)—C(6)—C(7) | 123·2 (3) | C(23)—C(18)—C(5) | 121·5 (3) |
| C(8)—C(7)—C(6) | 122·3 (4) | C(23)—C(18)—C(19) | 118·5 (3) |
| C(9)—C(8)—C(7) | 117·5 (4) | C(20)—C(19)—C(18) | 120·6 (3) |
| C(10)—C(9)—C(8) | 131·6 (4) | C(21)—C(20)—C(19) | 120·1 (3) |
| C(11)—C(10)—C(9) | 132·8 (4) | C(22)—C(21)—C(20) | 120·5 (3) |
| C(12)—C(11)—C(10) | 131·3 (3) | C(23)—C(22)—C(21) | 119·3 (4) |
| C(17)—C(12)—C(11) | 128·6 (3) | C(22)—C(23)—C(18) | 121·0 (4) |
| C(17)—C(13)—C(14) | 119·4 (2) | C(25)—C(24)—C(13) | 120·0 (2) |
| C(24)—C(13)—C(14) | 120·6 (2) | C(29)—C(24)—C(13) | 121·6 (2) |
| C(24)—C(13)—C(17) | 120·0 (2) | C(29)—C(24)—C(25) | 118·4 (2) |
| C(13)—C(14)—C(1) | 122·0 (2) | C(26)—C(25)—C(24) | 120·4 (3) |
| C(15)—C(14)—C(1) | 118·3 (2) | C(27)—C(26)—C(25) | 120·3 (3) |
| C(15)—C(14)—C(13) | 119·7 (2) | C(28)—C(27)—C(26) | 120·3 (3) |
| C(5)—C(15)—C(4) | 121·4 (2) | C(29)—C(28)—C(27) | 119·5 (3) |
| C(14)—C(15)—C(4) | 118·9 (2) | C(28)—C(29)—C(24) | 121·1 (3) |
| C(14)—C(15)—C(5) | 119·7 (2) | | |

(*c*) Endocyclic torsion angles for the nine-membered ring (°)

| | | | |
|---|---|---|---|
| C(17)—C(16)—C(6)—C(7) | −77·5 (5) | C(9)—C(10)—C(11)—C(12) | −48·4 (7) |
| C(16)—C(6)—C(7)—C(8) | −3·4 (7) | C(10)—C(11)—C(12)—C(17) | 3·4 (6) |
| C(6)—C(7)—C(8)—C(9) | 94·5 (8) | C(11)—C(12)—C(17)—C(16) | 79·3 (5) |
| C(7)—C(8)—C(9)—C(10) | −31·4 (8) | C(12)—C(17)—C(16)—C(6) | −7·4 (4) |
| C(8)—C(9)—C(10)—C(11) | 0·2 (8) | | |

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* Lists of coordinates and bond lengths and angles involving H atoms, together with structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38605 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The C atoms constituting each of the rings in the naphthalene unit lie within 0·01 Å of their respective least-squares planes, but there is evidence for slight (but statistically significant) non-planarity in the naphthalene segment as a whole, with naphthalene C atoms positioned up to 0·023 (4) Å from the least-squares plane. The evidence for the existence of steric congestion is reinforced by the magnitude of the C—Ph bond lengths, which at 1·495 (3) and 1·501 (3) Å for C(5)—C(18) and C(13)—C(24) respectively, are somewhat longer than the normal value of 1·486 Å.

The phenyl groups, which are planar within three standard deviations, and are oriented at angles of 63·2 (5)° [C(24) through C(29)], and 103·5 (5)° [C(18) through C(23)], to the naphthalene least-squares plane and 166·7° to each other, also show evidence of the effects of steric overcrowding, with internal ring angles at the C(24) and C(18) *ipso* C atoms of 118·4 (2) and 118·5 (3)° respectively.

The nine-membered ring adopts a distorted tub conformation, exhibiting strongly localized double bonds, high torsion angles about the single bonds and expansion of the internal ring angles. The tub lies on the same side of the naphthalene entity as the C(21)—C(22)—C(23)—C(18) and C(27)—C(28)—C(29)—C(24) fragments of the two phenyl rings, and the mean plane of the tub forms an angle of 45·2 (6)° with the naphthalene plane. The mirror plane which could be expected in the parent 9-annulene (at right angles to the molecular least-squares plane and along a line joining the $sp^3$ C with the midpoint of the opposite C—C single bond) is absent in (I), presumably due to the distorting influence of the ring annelation.

The intermolecular packing arrangement is determined by normal van der Waals contacts, with no interactions between the C atoms involving contact distances of less than 3·5 Å.

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*Acta Cryst.* (1983). C**39**, 1263–1267

# Structure of 2-(2-Hydroxy-1,1-dimethylethyl)-5,5-dimethyl-1,3-dioxan-4-ol, $C_{10}H_{20}O_4$, a Dimer of 3-Hydroxy-2,2-dimethylpropanal. Example of an Anhydrous Acetal Hydrolysis

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(*Received* 2 *February* 1983; *accepted* 9 *May* 1983)

**Abstract.** $M_r = 204·3$, monoclinic, $P2_1/c$, $a = 6·159\ (2)$, $b = 36·212\ (13)$, $c = 11·530\ (4)$ Å, $\beta = 116·86\ (1)°$, $V = 2294·1$ Å$^3$, $Z = 8$, $D_x = 1·18$, $D_m = 1·06$ Mg m$^{-3}$, $\lambda(\text{Cu } K\alpha_1) = 1·54051$ Å, $\mu = 0·75$ mm$^{-1}$, $F(000) = 896$, $T = 294$ K. Final $R = 0·053$ for 1405 observed reflections. There are two independent molecules per asymmetric unit, each one in a *cis* chair conformation. They lie on separate layers (*A* and *B*) in the crystal (perpendicular to **b**), with different hydrogen-bonding schemes in each layer. When melted, the dimer decomposes into the monomer, following an anhydrous acid-catalyzed acetal 'hydrolysis' mechanism. It is initiated by an *inter*molecular H-atom transfer which is assisted by a hydrogen bond in the *B* layer between the hydroxy group and a dioxane O atom on adjacent molecules. This decomposition is reversible, with the liquid monomer dimerizing on cooling. Attempts to form an orientationally disordered crystalline monomer by rapid cooling were unsuccessful.

**Introduction.** The title compound, hereafter referred to as $(R\text{CHO})_2$, was selected for investigation as part of our continuing study of polymorphism and orientational disorder in single crystals of pseudo-spherical molecules (Rudman, 1981; Sake Gowda & Rudman, 1982). The monomer of the title compound, hereafter

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