

1,1,2,3,4,5,6-Heptaphenyl-1,4-dihydrobenz[e]-as-indacene

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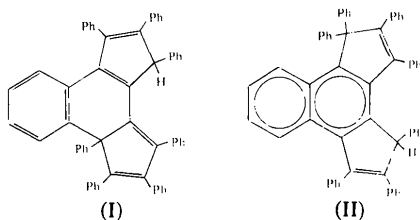
Abstract. $C_{58}H_{40}$, triclinic, $P\bar{1}$, $a = 10.041(2)$, $b = 11.916(2)$, $c = 18.264(4)$ Å, $\alpha = 77.85(2)$, $\beta = 104.74(2)$, $\gamma = 95.44(2)^\circ$, $V = 2064.0(4)$ Å³, $D_x = 1.186$, $D_m = 1.18$ Mg m⁻³ (floatation at 298 K), $Z = 2$. The structure was solved by direct methods using 5164 independent counter-diffractometer-measured reflections, and refined by block-diagonal least-squares methods to $R = 0.072$. The structure found is less strained than would be the case with any formulation previously suggested, but residual strain exists, leading to bond stretching and distortion of bond angles.

Introduction. The hydrocarbon $C_{58}H_{40}$ was first synthesized by Anschel (1967) by reaction of tetraphenylcyclopentadienone with triphenylphosphine. The NMR and mass spectrometric data suggested a structure different from that of the desired octaphenylfulvalene. From a study of organophosphorus intermediates in the synthetic reaction Gallagher & Jenkins (1969) proposed five possible structures represented by (I), the other four being derived by movement of the H atom shown to the other four positions in the upper five-membered ring, and rearrangement of the double bonds. Of these structures, that actually shown in (I) was favored on the basis of chemical behavior, and the ¹H NMR spectrum at 100 MHz. After further chemical work Borowitz, Anschel & Readio (1971) concurred that (I) was the most probable formula, but felt that, as it was not conclusively established, an X-ray structure deter-

mination should be carried out. The results of the crystallographic analysis are reported here, and establish the chemical structure to be (II).

A small crystal, approximately cube shaped and ~0.1 mm on edge, was used for measurement of the cell constants and for data collection. These were carried out on an Enraf-Nonius CAD-4 automated diffractometer with Ni-filtered radiation using the ω - 2θ scanning mode. The unit-cell parameters were refined by least squares from the angular settings of 15 high-angle reflections. Of 8774 independent reflections with $\theta < 70^\circ$, 5164 were accepted as observed according to the criterion $I > 1.5\sigma(I)$. Lorentz and polarization corrections were applied and structure amplitudes derived. Absorption corrections were not made [$\mu(\text{Cu } K\alpha) = 0.544$ mm⁻¹].

The structure was solved by direct methods, this and subsequent calculations being made using programs of the NRC system (Ahmed, Hall, Pippy & Huber, 1973). Refinement of the C atom positions and anisotropic thermal parameters was carried out by block-diagonal least-squares methods and the H atoms were then located from a difference electron density map. Refinement was then carried out on all positional parameters, anisotropic thermal parameters for the C atoms, and isotropic thermal parameters for the H atoms. Final refinement was made with the H atoms held in regularized positions at the average experimental distance of 0.99 Å from their bonded C atoms. In the final cycle $R = 0.072$ and $R_w = 0.060$ for observed reflections only, and $R = 0.098$ for all reflections.† The mean and maximum shift/e.s.d. values were 0.066 and 0.212 and $[\sum w|\Delta F|^2/(m - n)]^{1/2} = 0.986$. The function minimized was $\sum w(|F_o| - k|F_c|)^2$ where w was obtained from the counting statistics. Unobserved reflections were weighted zero. The scattering factors



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† Lists of H atom parameters, anisotropic thermal parameters, bond angles and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35215 (57 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) for the carbon atoms

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	2675 (4)	7867 (3)	8140 (2)
C(2)	2401 (3)	8874 (3)	8490 (2)
C(3)	2292 (3)	9864 (3)	7967 (2)
C(4)	2440 (4)	11671 (3)	6305 (2)
C(5)	2375 (4)	11879 (3)	5449 (2)
C(6)	2442 (4)	10899 (3)	5216 (2)
C(7)	2680 (4)	8244 (3)	5303 (2)
C(8)	2860 (4)	7102 (3)	5394 (2)
C(9)	2952 (5)	6373 (3)	6112 (2)
C(10)	2857 (4)	6806 (3)	6729 (2)
C(11)	2686 (4)	7987 (3)	6673 (2)
C(12)	2585 (4)	8471 (3)	7302 (2)
C(13)	2434 (3)	9633 (3)	7228 (2)
C(14)	2430 (3)	10377 (3)	6519 (2)
C(15)	2486 (3)	9928 (3)	5883 (2)
C(16)	2605 (3)	8735 (3)	5934 (2)
C(17)	1543 (4)	6922 (3)	8252 (2)
C(18)	396 (4)	6793 (4)	7670 (3)
C(19)	-672 (5)	6007 (4)	7809 (3)
C(20)	-573 (5)	5336 (4)	8527 (3)
C(21)	568 (6)	5433 (4)	9100 (3)
C(22)	1619 (5)	6227 (3)	8978 (2)
C(23)	4175 (4)	7481 (3)	8505 (2)
C(24)	4524 (5)	6350 (4)	8687 (3)
C(25)	5896 (6)	6071 (5)	9001 (3)
C(26)	6896 (5)	6913 (6)	9129 (3)
C(27)	6575 (5)	8038 (5)	8949 (3)
C(28)	5216 (4)	8324 (4)	8632 (2)
C(29)	2192 (4)	8721 (3)	9281 (2)
C(30)	3252 (4)	8515 (5)	9928 (3)
C(31)	3008 (5)	8372 (5)	10659 (2)
C(32)	1698 (5)	8404 (5)	10745 (2)
C(33)	649 (5)	8596 (5)	10112 (3)
C(34)	887 (4)	8761 (4)	9382 (2)
C(35)	2070 (4)	11000 (3)	8132 (2)
C(36)	3031 (5)	11434 (4)	8705 (2)
C(37)	2855 (6)	12484 (4)	8867 (3)
C(38)	1741 (6)	13097 (4)	8474 (3)
C(39)	760 (5)	12681 (4)	7902 (3)
C(40)	925 (4)	11625 (3)	7730 (2)
C(41)	3753 (4)	12247 (3)	6730 (2)
C(42)	5018 (4)	11807 (4)	6800 (3)
C(43)	6208 (5)	12349 (4)	7153 (3)
C(44)	6166 (6)	13311 (4)	7436 (3)
C(45)	4923 (6)	13756 (4)	7368 (3)
C(46)	3710 (5)	13221 (3)	7011 (2)
C(47)	2259 (4)	13057 (3)	4961 (2)
C(48)	1029 (5)	13566 (4)	4727 (3)
C(49)	885 (6)	14638 (4)	4249 (3)
C(50)	1987 (5)	15196 (4)	4018 (3)
C(51)	3225 (5)	14720 (4)	4250 (3)
C(52)	3370 (5)	13651 (4)	4728 (3)
C(53)	2456 (4)	10837 (3)	4417 (2)
C(54)	3677 (4)	10995 (4)	4178 (2)
C(55)	3675 (5)	10985 (5)	3423 (3)
C(56)	2473 (5)	10827 (4)	2898 (2)
C(57)	1269 (4)	10683 (4)	3127 (2)
C(58)	1255 (4)	10686 (4)	3876 (2)

used were that of Cromer & Waber (1965) for C and that of Stewart, Davidson & Simpson (1965) for H. The refined positional parameters for the C atoms are given in Table 1. The bond distances, corrected for

Table 2. Bond distances (\AA) involving carbon atoms

C(1)—C(2)	1.552 (5)	C(29)—C(30)	1.373 (5)
C(2)—C(3)	1.349 (5)	C(30)—C(31)	1.392 (6)
C(3)—C(13)	1.479 (5)	C(31)—C(32)	1.372 (8)
C(13)—C(12)	1.385 (5)	C(32)—C(33)	1.350 (7)
C(12)—C(1)	1.534 (5)	C(33)—C(34)	1.385 (6)
C(13)—C(14)	1.409 (5)	C(34)—C(29)	1.379 (6)
C(14)—C(15)	1.396 (5)	C(3)—C(35)	1.499 (5)
C(15)—C(16)	1.423 (5)	C(35)—C(36)	1.386 (6)
C(16)—C(11)	1.443 (5)	C(36)—C(37)	1.385 (7)
C(11)—C(12)	1.421 (5)	C(37)—C(38)	1.355 (8)
C(16)—C(7)	1.421 (5)	C(38)—C(39)	1.385 (8)
C(7)—C(8)	1.363 (6)	C(39)—C(40)	1.397 (7)
C(8)—C(9)	1.401 (6)	C(40)—C(35)	1.388 (6)
C(9)—C(10)	1.364 (6)	C(4)—C(41)	1.534 (5)
C(10)—C(11)	1.417 (5)	C(41)—C(42)	1.388 (5)
C(14)—C(4)	1.512 (5)	C(42)—C(43)	1.381 (7)
C(4)—C(5)	1.517 (5)	C(43)—C(44)	1.365 (7)
C(5)—C(6)	1.341 (5)	C(44)—C(45)	1.371 (8)
C(6)—C(15)	1.490 (5)	C(45)—C(46)	1.396 (7)
C(1)—C(17)	1.546 (5)	C(46)—C(41)	1.377 (6)
C(17)—C(18)	1.379 (6)	C(5)—C(47)	1.496 (5)
C(18)—C(19)	1.396 (7)	C(47)—C(48)	1.360 (6)
C(19)—C(20)	1.372 (7)	C(48)—C(49)	1.387 (7)
C(20)—C(21)	1.359 (8)	C(49)—C(50)	1.353 (8)
C(21)—C(22)	1.381 (7)	C(50)—C(51)	1.349 (8)
C(22)—C(17)	1.398 (6)	C(51)—C(52)	1.385 (7)
C(1)—C(23)	1.558 (5)	C(52)—C(47)	1.378 (6)
C(23)—C(24)	1.379 (6)	C(6)—C(53)	1.483 (5)
C(24)—C(25)	1.397 (8)	C(53)—C(54)	1.389 (6)
C(25)—C(26)	1.366 (9)	C(54)—C(55)	1.383 (6)
C(26)—C(27)	1.364 (9)	C(55)—C(56)	1.365 (6)
C(27)—C(28)	1.388 (6)	C(56)—C(57)	1.364 (6)
C(28)—C(23)	1.393 (6)	C(57)—C(58)	1.375 (5)
C(2)—C(29)	1.486 (5)	C(58)—C(53)	1.378 (5)

librational effects (Schomaker & Trueblood, 1968), are given in Table 2. These corrections were small, in the range 0.002–0.004 \AA , and the r.m.s. ΔU_{ij} was 0.0123 \AA^2 .

Discussion. The numbering scheme used is shown in Fig. 1 and a stereoscopic view of one unit cell (Johnson, 1965) in Fig. 2. The structure found is less strained than any of those previously postulated. However, some crowding still exists. The distances C(22)—C(24), C(22)—C(29) and C(18)—C(10) are 3.081, 3.110 and 3.347 \AA respectively. These interactions would be more severe were it not for the stretching of the bonds C(1)—C(2), C(1)—C(17) and C(1)—C(23), the average of which is 12σ longer than the standard sp^2 — sp^3 value of 1.515 \AA (Dewar & Schmeising, 1960), and the widening of certain bond angles, notably C(17)—C(1)—C(23) and C(17)—C(1)—C(12) which are 114.9 (3) and 115.0 (3) $^\circ$ respectively.

The tetracyclic nucleus shows significant deviations from planarity, the largest displacements from the least-squares mean plane occurring at the reduced positions C(1) (–0.083 \AA) and C(4) (–0.129 \AA). The naphthalene nucleus itself shows deviations of up to 0.04 \AA from planarity. The four phenyl rings *G*, *H*, *J*

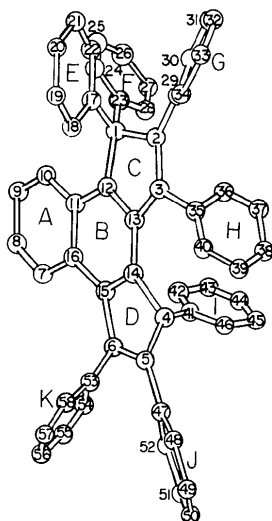


Fig. 1. The atomic numbering scheme used.

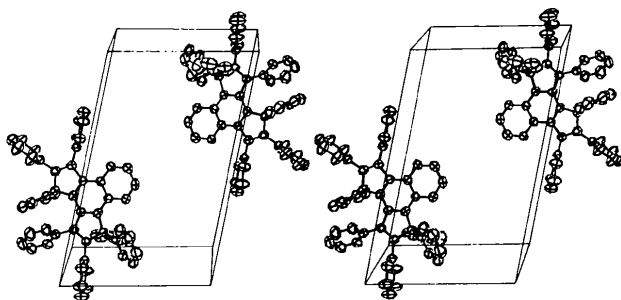


Fig. 2. A stereoscopic diagram of the contents of one unit cell.

and K, which are connected to the nucleus by sp^2-sp^2 bonds, make large dihedral angles, in the range $59-86^\circ$, with the five-membered rings to which they are bonded (Figs. 1 and 2).

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D,L-3-Amino-1-hydroxy-2-pyrrolidone Trihydrate (D,L-HA-966)

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Abstract. $C_4H_8N_2O_2 \cdot 3H_2O$, $M_r = 170.2$, monoclinic, $P2_1/c$, $a = 11.86$ (8), $b = 6.84$ (14), $c = 11.73$ (14) Å, $\beta = 114.94$ (2)°, $U = 863$ Å³, $D_x = 1.31$ Mg m⁻³, $Z = 4$; final $R = 0.056$ for 977 unique reflections. The compound exists as a zwitterion in the crystal. The pyrrolidine ring has an almost perfect envelope

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In the naphthalene system the distances in ring A are very close to those measured and calculated by molecular-orbital methods in naphthalene itself (Cruikshank & Sparks, 1960). However, in ring B the bond character appears to be modified by fusion with the five-membered rings. Throughout the rest of the molecule bond distances and angles, other than those noted above, appear normal.

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References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1973). NRC Crystallographic Programs for the IBM/360 System. Accession Nos. 133–147 in *J. Appl. Cryst.* **6**, 309–346.
- ANSHEL, M. A. (1967). PhD Thesis, Lehigh Univ., Bethlehem, PA, USA.
- BOROWITZ, I. J., ANSHEL, M. A. & READIO, P. D. (1971). *J. Org. Chem.* **36**, 553–560.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- CRUICKSHANK, D. W. J. & SPARKS, R. A. (1960). *Proc. R. Soc. London Ser. A*, **258**, 270–285.
- DEWAR, M. J. S. & SCHMEISING, H. N. (1960). *Tetrahedron*, **11**, 96–120.
- GALLAGHER, M. J. & JENKINS, I. D. (1969). *J. Chem. Soc.* pp. 2605–2614.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

conformation and very little hydrogen bonding occurs between the water molecules and the HA-966 molecules.

Introduction. The title compound has been reported as a selective antagonist at the physiological aspartate

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