

would utilize O(4' $\alpha$ ) are available including the formation of dimers across a center of symmetry between N(3') and the C(4') substituent, a common scheme in thiamin structures.

The comparison between oxythiamin and thiamin again draws attention to the uniqueness of the pyrimidine ring in thiamin among the biologically active pyrimidine compounds. Its unique character results primarily from having a 2'-methyl substituent instead of the 2'-oxo of the pyrimidine nucleotides. Although this required methyl substituent may serve simply to distinguish this coenzyme from the pyrimidine nucleotides, it may have a functional role as well in establishing the necessary electronic conditions. The unusual exchange and bonding properties of this methyl group (Hutchinson, 1971; Pletcher & Sax, 1972) are certainly consistent with a functional involvement.

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## Structures of Dibenzo[*a,e*]cyclooctatetraene and Tetrabenzo[*a,c,e,g*]cyclooctatetraene (*o*-Tetraphenylene)

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#### Abstract

The structures of dibenzo[*a,e*]cyclooctatetraene, C<sub>16</sub>H<sub>12</sub>, *M<sub>r</sub>* = 204.3, (I) and tetrabenzo[*a,c,e,g*]cyclooctatetraene, C<sub>24</sub>H<sub>16</sub>, *M<sub>r</sub>* = 304.4, (II) are described. (I) crystallizes in the monoclinic space group *P2<sub>1</sub>/n* with *a* = 11.605 (2), *b* = 7.849 (1), *c* = 12.282 (2) Å,  $\beta$  = 95.33 (1)°, *Z* = 4, *D<sub>x</sub>* = 1.22 Mg

m<sup>-3</sup>, m.p. = 504–505 K. (II) crystallizes in the monoclinic space group *C2/c* with *a* = 15.628 (6), *b* = 13.126 (2), *c* = 16.369 (4) Å,  $\beta$  = 100.56 (4)°, *Z* = 8, *D<sub>x</sub>* = 1.23 Mg m<sup>-3</sup>, m.p. = 380–381 K. The structures were refined to *R* = 0.044 for (I) and 0.047 for (II) for 2093 and 2997 unique reflections respectively. Both molecules have a tub shape and are more rigid than cyclooctatetraene.

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## Introduction

Cyclooctatetraene and its derivatives have a tub-shaped structure (Fray & Saxton, 1978; Schröder, 1965). Many attempts have been described to produce a planar arrangement of the dibenzo[*a,e*]cyclooctatetraene (I) (*sym*-dibenzocyclooctatetraene) and tetrabenzo[*a,c,e,g*]cyclooctatetraene (II) (*o*-tetraphenylene) systems.

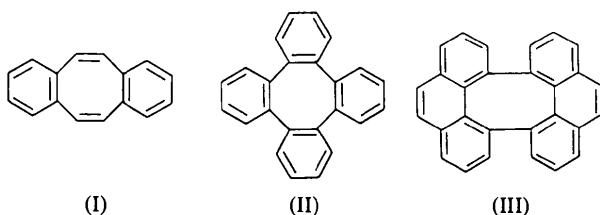
Planar structures of the radical anions (Kojima, Bard, Wong & Sondheimer, 1976; Gerson, Martin, Plattner & Sondheimer, 1976), dianions (Günther, 1978) and dications (Olah, Staral, Liang, Paquette, Melega & Carmody, 1977) of (I) follow from their properties. The geometry of the anion of (II) could not be proved unequivocally (Garst, 1965; Carrington, Longuet-Higgins & Todd, 1965).

The inversion barrier through a planar transition state is of the order of 50 kJ mol<sup>-1</sup> for (I) (Senkler, Gust, Riccobono & Mislow, 1972). The corresponding value of (II) exceeds 189 kJ mol<sup>-1</sup> because of strong non-bonded interactions of H atoms (Gust, Senkler & Mislow, 1972; Rosdahl & Sandström, 1972).

The dehydro derivatives of (I) with one or two triple bonds are planar (Destro, Pilati & Simonetta, 1975; Au, Siu, Mak & Chan, 1978).

Derivatives of (II) with O atom (Berg, Erdtman, Högberg, Karlsson & Pilotti, 1977) and C atom bridges (Hellwinkel, Reiff & Nykodym, 1977; Hellwinkel & Haas, 1979) in the *ortho* position to the eight-membered ring were synthesized to force the molecular system (II) into a more planar arrangement. The dibenzo[*def,pqr*]tetraphenylene (III) (bi-4,5-phenanthrylene) with only two bridges is far from planar (Irngartinger, Reibel & Sheldrick, 1981).

We determined the structure of (I) and (II) to clarify the detailed ground-state geometry of these unsubstituted molecules. An electron diffraction study of (II) indicated a tub shape (Karle & Brockway, 1944).



## Experimental

(I) and (II) were synthesized by known methods [(I): Cope & Fenton, 1951; (II): Lindow & Friedman, 1967]. Single crystals were obtained by evaporating a CCl<sub>4</sub> solution of (I) and by cooling an ethanol solution of (II). The cell dimensions were derived by least squares from high-order reflections ( $2\theta \geq 46^\circ$ ) measured on a diffractometer with Mo *K* $\alpha$  radiation.

Table 1. Data collection parameters

	(I)	(II)
Crystal dimensions (mm)	0.45 × 0.30 × 0.30	0.15 × 0.17 × 0.54
Maximum $\sin \theta/\lambda$ (Å <sup>-1</sup> )	0.664	0.664
Number of unique reflections	2833	3036
Number of unobserved reflections	995	1284
Criterion for unobserved reflections	$F_o^2 < 2.24\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$
Number of unobserved reflections used in the refinement ( $ F_c  > k \cdot F_o$ )	268	262
Number of reflections given zero weight (extinction errors)	13	17
Final <i>R</i> (without unobserved reflections)	0.044	0.047
Final <i>R</i> (including unobserved reflections)	0.052	0.055

The crystal data of (II) are in agreement with the values of Rapson, Shuttleworth & van Niekerk (1943). The intensities were collected on a computer-controlled diffractometer (Siemens AED, Mo *K* $\alpha$  radiation, graphite monochromator,  $\theta/2\theta$  scan). Details of data collection are given in Table 1. Lorentz and polarization corrections were applied.

## Structure determination and refinement

The structures were solved with *MULTAN* (Germain, Main & Woolfson, 1971). *E* maps computed with the phase sets which had the highest figures of merit revealed the molecular skeleton.

The H atoms were inserted in chemically reasonable positions. In the final cycle the C atoms were refined anisotropically and the H atoms isotropically by full-matrix least squares.  $R = \sum |kF_o - |F_c|| / \sum kF_o$  and further details of refinement are found in Table 1. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

The atomic coordinates of (I) and (II) are listed in Tables 2 and 3, and bond lengths and angles in Tables 4 and 5.\* The atoms are labelled in the *ORTEP* (Johnson, 1976) drawings, Figs. 1 and 2. All calcula-

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35940 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

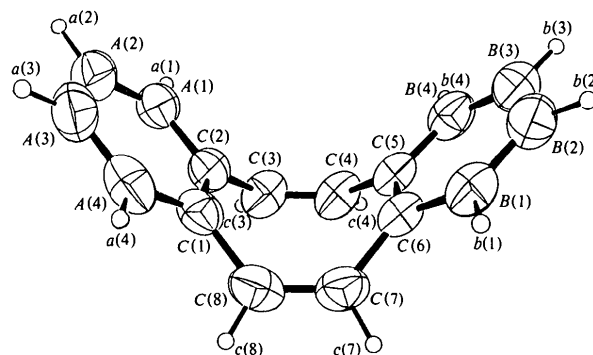
Fig. 1. *ORTEP* drawing of (I) with the atom labels.

Table 2. Atomic coordinates of (I) ( $\times 10^5$  for C and  $\times 10^4$  for H) and isotropic thermal parameters ( $U_{eq}$ ,  $\times 10^4$ , for C and  $U_{iso}$ ,  $\times 10^3$ , for H) with e.s.d.'s in parentheses (see Fig. 1 for atomic notation; a–c represent H atoms)

$U_{eq} = (U_1 U_2 U_3)^{1/3}$  (F. R. Ahmed, 1979, private communication);  $\sigma(U_{eq}) = [k\sigma(U_{ii}) \cdot U_{eq}] / (\langle U_{ii} \rangle \cdot \sqrt{6})$  (V. Schomaker, 1980, private communication).

	x	y	z	$U_{eq}/U_{iso}$ ( $\text{\AA}^2$ )
C(1)	−6448 (12)	26019 (18)	36698 (12)	542 (3)
C(2)	−15772 (11)	37073 (18)	34487 (11)	526 (3)
C(3)	−21328 (13)	40145 (22)	23382 (12)	617 (4)
C(4)	−16627 (13)	46900 (22)	14980 (13)	610 (4)
C(5)	−4569 (11)	52618 (19)	14683 (10)	507 (3)
C(6)	4976 (11)	41983 (18)	16986 (10)	506 (3)
C(7)	3977 (14)	23802 (21)	19748 (14)	616 (4)
C(8)	−844 (14)	17003 (22)	28046 (14)	646 (4)
A(1)	−20591 (14)	44984 (21)	43193 (12)	604 (4)
A(2)	−16313 (16)	42139 (24)	53834 (13)	687 (4)
A(3)	−7267 (17)	31170 (24)	56066 (14)	692 (4)
A(4)	−2402 (16)	23080 (22)	47638 (14)	652 (4)
B(1)	16026 (13)	48500 (22)	16015 (12)	590 (4)
B(2)	17761 (16)	65096 (23)	13053 (12)	660 (4)
B(3)	8347 (16)	75509 (24)	10645 (13)	692 (4)
B(4)	−2605 (16)	69261 (22)	11302 (12)	630 (4)
c(3)	−2942 (13)	3782 (19)	2240 (11)	65 (4)
c(4)	−2152 (12)	4985 (18)	846 (12)	63 (4)
c(7)	796 (13)	1647 (21)	1506 (13)	75 (5)
c(8)	−10 (13)	527 (22)	2920 (12)	75 (5)
a(1)	−2741 (14)	5263 (21)	4146 (12)	74 (5)
a(2)	−1974 (13)	4839 (21)	6027 (14)	81 (5)
a(3)	−413 (16)	2925 (22)	6333 (16)	89 (6)
a(4)	400 (13)	1555 (20)	4883 (12)	66 (5)
b(1)	2261 (13)	4089 (20)	1759 (11)	63 (4)
b(2)	2552 (14)	6934 (20)	1245 (12)	72 (5)
b(3)	956 (15)	8714 (23)	808 (14)	86 (5)
b(4)	−932 (14)	7614 (20)	937 (12)	70 (5)

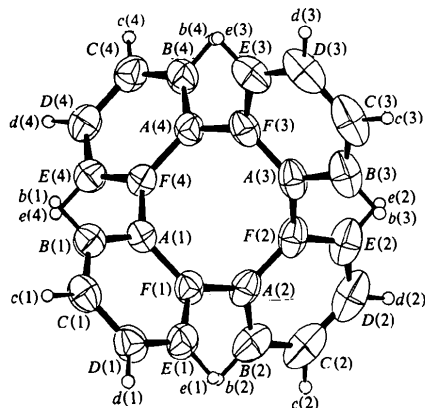


Fig. 2. ORTEP drawing of (II) with the atom labels.

tions were carried out in the computer centre of the University of Heidelberg (IBM 370-168).

### Discussion

Chemically equivalent bond lengths and angles are averaged in Table 6. The scatter values  $s$  are of the

order of the e.s.d.'s of the individual measurements. Compared to the double bond of cyclooctatetraene (COT), the analogous bonds  $a$  of (I) and (II) are longer because of condensation of benzene rings to the COT skeleton (Table 6). The bond  $f$  in (I) is comparatively short. As a consequence of additional 1...3 repulsive interactions of C atoms, the  $C(sp^2)-C(sp^2)$  single bond  $b$  of (II) is longer than in (I) and in COT. The benzene rings make the eight-membered ring more rigid. Whereas the bond angles are opened up in (I) ( $127.6^\circ$ ) and COT ( $126.9, 126.1^\circ$ ), the angles  $\delta$  of (I) and (II) are in the range  $122-123^\circ$ . From the magnitude of the torsion angles (Table 7) of  $66.1$  (II),

Table 3. Atomic coordinates of (II) ( $\times 10^4$  for C and  $\times 10^3$  for H) and isotropic thermal parameters ( $U_{eq}$ ,  $\times 10^4$ , for C and  $U_{iso}$ ,  $\times 10^3$ , for H) with e.s.d.'s in parentheses (see Fig. 2 for atomic notation; a–e represent H atoms)

Definition of  $U_{eq}$  and  $\sigma(U_{eq})$  as in Table 2.

	x	y	z	$U_{eq}/U_{iso}$ ( $\text{\AA}^2$ )
A(1)	2068 (1)	4538 (2)	2014 (1)	397 (4)
B(1)	1190 (2)	4308 (2)	1981 (2)	571 (8)
C(1)	542 (2)	4759 (2)	1408 (2)	655 (8)
D(1)	757 (2)	5446 (2)	849 (2)	585 (8)
E(1)	1623 (2)	5675 (2)	860 (1)	479 (5)
F(1)	2288 (1)	5234 (2)	1438 (1)	384 (4)
A(2)	3199 (1)	5583 (2)	1454 (1)	363 (4)
B(2)	3386 (2)	6620 (2)	1549 (1)	451 (5)
C(2)	4202 (2)	6994 (2)	1515 (1)	513 (8)
D(2)	4856 (2)	6346 (2)	1394 (1)	515 (7)
E(2)	4685 (2)	5310 (2)	1292 (1)	449 (6)
F(2)	3859 (1)	4916 (2)	1314 (1)	363 (4)
A(3)	3689 (1)	3912 (2)	1116 (1)	377 (4)
B(3)	3800 (1)	3460 (2)	338 (1)	454 (7)
C(3)	3699 (2)	2444 (2)	133 (2)	521 (8)
D(3)	3494 (2)	1755 (2)	703 (2)	542 (8)
E(3)	3387 (2)	2088 (2)	1475 (1)	500 (8)
F(3)	3475 (1)	3115 (2)	1693 (1)	383 (4)
A(4)	3382 (1)	3424 (1)	2549 (1)	379 (4)
B(4)	3938 (2)	2991 (2)	3227 (1)	463 (8)
C(4)	3858 (2)	3216 (2)	4033 (1)	518 (8)
D(4)	3221 (2)	3874 (2)	4179 (2)	512 (6)
E(4)	2658 (2)	4306 (2)	3518 (1)	502 (6)
F(4)	2729 (1)	4090 (1)	2697 (1)	394 (4)
b(1)	104 (2)	380 (2)	239 (1)	71 (8)
c(1)	−7 (2)	458 (2)	143 (1)	78 (8)
d(1)	33 (1)	579 (2)	44 (1)	58 (7)
e(1)	178 (1)	617 (1)	47 (1)	46 (6)
b(2)	292 (1)	708 (2)	161 (1)	51 (7)
c(2)	430 (1)	772 (2)	155 (1)	56 (7)
d(2)	548 (1)	663 (2)	140 (1)	53 (7)
e(2)	514 (1)	486 (2)	118 (1)	52 (7)
b(3)	399 (1)	394 (2)	−7 (1)	49 (6)
c(3)	373 (1)	223 (2)	−43 (1)	53 (7)
d(3)	343 (1)	103 (2)	56 (1)	60 (7)
e(3)	323 (1)	162 (2)	191 (1)	55 (7)
b(4)	441 (2)	253 (2)	314 (1)	67 (8)
c(4)	427 (1)	292 (2)	450 (1)	57 (7)
d(4)	318 (1)	403 (2)	473 (1)	59 (7)
e(4)	219 (1)	475 (2)	362 (1)	45 (6)

Table 4. Bond lengths (Å)

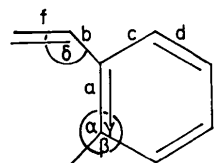
(I)			
C(1)—C(2)	1.394 (2)	C(5)—C(6)	1.395 (2)
C(3)—C(4)	1.321 (2)	C(7)—C(8)	1.320 (2)
C(2)—C(3)	1.474 (2)	C(4)—C(5)	1.473 (2)
C(6)—C(7)	1.474 (2)	C(1)—C(8)	1.477 (2)
C(2)—A(1)	1.397 (2)	C(1)—A(4)	1.401 (2)
C(6)—B(1)	1.396 (2)	C(5)—B(4)	1.396 (2)
A(1)—A(2)	1.373 (2)	A(3)—A(4)	1.379 (3)
B(1)—B(2)	1.372 (3)	B(3)—B(4)	1.372 (3)
A(2)—A(3)	1.366 (3)	B(2)—B(3)	1.374 (3)
(II)			
A(1)—F(1)	1.399 (3)	A(2)—F(2)	1.403 (3)
A(3)—F(3)	1.399 (3)	A(4)—F(4)	1.399 (3)
A(1)—F(4)	1.497 (2)	A(2)—F(1)	1.491 (3)
A(3)—F(2)	1.497 (3)	A(4)—F(3)	1.490 (3)
A(1)—B(1)	1.397 (3)	E(1)—F(1)	1.397 (3)
A(2)—B(2)	1.394 (3)	E(2)—F(2)	1.398 (3)
A(3)—B(3)	1.394 (3)	E(3)—F(3)	1.395 (3)
A(4)—B(4)	1.399 (3)	E(4)—F(4)	1.398 (3)
B(1)—C(1)	1.381 (4)	D(1)—E(1)	1.382 (4)
B(2)—C(2)	1.378 (4)	D(2)—E(2)	1.390 (3)
B(3)—C(3)	1.377 (3)	D(3)—E(3)	1.377 (4)
B(4)—C(4)	1.380 (3)	D(4)—E(4)	1.385 (3)
C(1)—D(1)	1.370 (4)	C(2)—D(2)	1.371 (4)
C(3)—D(3)	1.378 (4)	C(4)—D(4)	1.371 (4)

Table 5. Bond angles (°)

(I)			
C(1)—C(2)—C(3)	123.3 (1)	C(2)—C(1)—C(8)	122.9 (1)
C(4)—C(5)—C(6)	123.4 (1)	C(5)—C(6)—C(7)	123.2 (1)
C(2)—C(3)—C(4)	127.7 (1)	C(3)—C(4)—C(5)	127.1 (1)
C(6)—C(7)—C(8)	128.1 (2)	C(1)—C(8)—C(7)	127.5 (2)
C(2)—C(1)—A(4)	118.3 (1)	C(1)—C(2)—A(1)	119.1 (1)
C(5)—C(6)—B(1)	118.8 (1)	C(6)—C(5)—B(4)	118.2 (1)
C(2)—A(1)—A(2)	121.4 (1)	C(1)—A(4)—A(3)	121.3 (2)
C(5)—B(4)—B(3)	122.0 (2)	C(6)—B(1)—B(2)	121.9 (1)
A(1)—A(2)—A(3)	119.8 (2)	A(2)—A(3)—A(4)	120.0 (2)
B(1)—B(2)—B(3)	119.2 (2)	B(2)—B(3)—B(4)	119.8 (2)
C(3)—C(2)—A(1)	117.6 (1)	C(4)—C(5)—B(4)	118.3 (1)
C(7)—C(6)—B(1)	117.8 (1)	C(8)—C(1)—A(4)	118.7 (1)
(II)			
F(1)—A(1)—F(4)	122.6 (1)	A(1)—F(1)—A(2)	122.7 (2)
F(1)—A(2)—F(2)	122.2 (2)	A(2)—F(2)—A(3)	122.2 (2)
F(2)—A(3)—F(3)	122.7 (2)	A(3)—F(3)—A(4)	122.3 (2)
F(3)—A(4)—F(4)	122.2 (2)	A(4)—F(4)—A(1)	122.8 (2)
B(1)—A(1)—F(4)	118.8 (2)	E(1)—F(1)—A(2)	118.3 (2)
B(2)—A(2)—F(1)	118.7 (2)	E(2)—F(2)—A(3)	118.7 (2)
B(3)—A(3)—F(2)	118.1 (2)	E(3)—F(3)—A(4)	118.7 (2)
B(4)—A(4)—F(3)	118.9 (2)	E(4)—F(4)—A(1)	118.2 (2)
B(1)—A(1)—F(1)	118.5 (2)	A(1)—F(1)—E(1)	118.8 (2)
B(2)—A(2)—F(2)	118.8 (2)	A(2)—F(2)—E(2)	118.9 (2)
B(3)—A(3)—F(3)	119.0 (2)	A(3)—F(3)—E(3)	119.0 (2)
B(4)—A(4)—F(4)	118.0 (2)	A(4)—F(4)—E(4)	118.9 (2)
A(1)—B(1)—C(1)	121.7 (3)	D(1)—E(1)—F(1)	121.6 (2)
A(2)—B(2)—C(2)	121.3 (2)	D(2)—E(2)—F(2)	121.1 (2)
A(3)—B(3)—C(3)	121.0 (2)	D(3)—E(3)—F(3)	121.2 (2)
A(4)—B(4)—C(4)	121.4 (2)	D(4)—E(4)—F(4)	121.1 (2)
B(1)—C(1)—D(1)	119.8 (3)	C(1)—D(1)—E(1)	119.6 (2)
B(2)—C(2)—D(2)	120.3 (2)	C(2)—D(2)—E(2)	119.5 (3)
B(3)—C(3)—D(3)	120.1 (2)	C(3)—D(3)—E(3)	119.7 (2)
B(4)—C(4)—D(4)	119.8 (2)	C(4)—D(4)—E(4)	120.0 (2)

Table 6. Averaged bond lengths (Å) and angles (°)

The scatter  $s = [\sum (x - \sum x/n)^2 / (n - 1)]^{1/2}$  is given in parentheses. The  $x$  values are the data and  $n$  is the number of data to be averaged. The data for cyclooctatetraene (COT) are determined by X-ray diffraction (XR) (Bregman & Post, private communication, quoted in Bordner, Parker & Stanford, 1972) and electron diffraction (ED) (Trætterberg, 1966).



	(I)	(II)	COT (XR)	COT (ED)
<i>a</i>	1.395 (1)	1.400 (2)	—	—
<i>b</i>	1.475 (2)	1.494 (4)	1.453	1.476
<i>c</i>	1.398 (2)	1.397 (2)	—	—
<i>d</i>	1.374 (3)	1.381 (4)	—	—
<i>e</i>	1.370 (6)	1.373 (4)	—	—
<i>f</i>	1.321 (1)	—	1.331	1.340
$\alpha$	123.2 (2)	122.5 (3)	—	—
$\beta$	118.1 (5)	118.6 (3)	—	—
$\gamma$	118.6 (4)	118.8 (2)	—	—
$\delta$	127.6 (4)	—	126.9	126.1

Table 7. Torsion angles (°)

(I)			
C(1)—C(2)—C(3)—C(4)	-62.6 (3)	C(2)—C(3)—C(4)—C(5)	1.2 (3)
C(3)—C(4)—C(5)—C(6)	58.1 (2)	C(4)—C(5)—C(6)—C(7)	1.3 (2)
C(5)—C(6)—C(7)—C(8)	-60.4 (2)	C(6)—C(7)—C(8)—C(1)	-0.2 (3)
C(7)—C(8)—C(1)—C(2)	57.7 (2)	C(8)—C(1)—C(2)—C(3)	3.2 (2)
Mean	59.7 (2.3)		1.5 (1.3)
(II)			
A(1)—F(1)—A(2)—F(2)	64.5 (3)	F(1)—A(2)—F(2)—A(3)	1.7 (3)
A(2)—F(2)—A(3)—F(3)	-68.2 (3)	F(2)—A(3)—F(3)—A(4)	1.2 (3)
A(3)—F(3)—A(4)—F(4)	64.9 (3)	F(3)—A(4)—F(4)—A(1)	0.6 (3)
A(4)—F(4)—A(1)—F(1)	-66.9 (3)	F(4)—A(1)—F(1)—A(2)	0.4 (3)
Mean	66.1 (1.7)		1.0 (6)

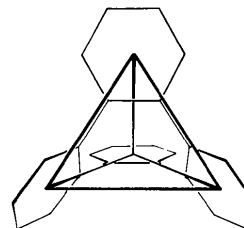


Fig. 3. Tetrahedron constructed by the connecting lines between the centres of the benzene rings of (II).

59.7 (I) and 54.9° (COT, Bregman & Post, private communication, quoted in Bordner, Parker & Stanford, 1972), it follows that the eight-membered rings of these compounds become flatter in the given sequence. The average dihedral angle between the phenyl rings in (II) is 62 (2)°. The centres of gravity of the benzene rings of (II) are the corners of a tetrahedron (Fig. 3).

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## SHORT STRUCTURAL PAPERS

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### Dodecacarbonyltetra- $\mu$ -hydrido-tetrahedro-tetraosmium

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**Abstract.** [Os<sub>4</sub>(CO)<sub>12</sub>H<sub>4</sub>], triclinic,  $P\bar{1}$ ,  $a = 9.811$  (3),  $b = 9.893$  (3),  $c = 10.240$  (4) Å,  $\alpha = 85.56$  (2),  $\beta = 82.71$  (2),  $\gamma = 88.71$  (2)°,  $U = 982.82$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 3.72$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 25.83$  mm<sup>-1</sup>. The structure refined to  $R = 0.043$  for 1815 unique diffractometer data. The Os atoms define a distorted tetrahedron with approximate  $D_{2d}$  symmetry, there being four long and two short metal–metal bonds. Each Os atom is

coordinated to three terminal carbonyls. The arrangement of these groups indicates that the four hydrides edge-bridge the four long Os–Os bonds. The molecules pack in a disordered manner about a molecular centre of symmetry in a ratio of 19 : 1.

**Introduction.** A knowledge of the molecular geometry of the hydrido-carbonyl clusters of the type