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CRYSTAL STRUCTURE AND CONFORMATION OF BIS-(TRICARBONYLIRON)HEPTALENE

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Summary

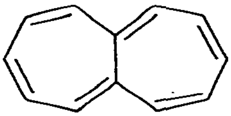
$Fe_2C_{18}O_6H_{10}$ is monoclinic, space group $P2_1/n$ with $a = 12.517$, $b = 12.661$, $c = 10.632$ Å, $\beta = 90.92°$, $Z = 4$. The structure was refined to $R = 0.024$ for 2702 counter reflections. The two outer butadiene moieties are *exo* complexed with tricarbonyliron units, thus forming tetragonal pyramidal iron complexes. The seven-membered rings of the heptalene have boat conformations with a flat central region and structure angles $\alpha = 6°$ and $\beta = 41°$. The molecules are packed in chains along the a-direction with shortest intermolecular distances between carbonyl units.

Introduction

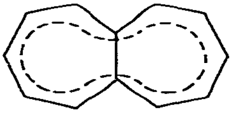
Many experimental and theoretical studies have concerned the molecular properties of heptalene (I) [1,2]. Its 12π-electron system is suggested to consist of localized double bonds (Ia) rather than a delocalized structure (Ib). The barrier for the valence isomerization has been calculated to be 6—7 kcal (25—29 kJ)/mol [3]. Müllen et al. [4] found evidence for an internal barrier of 3.5 kcal (15 kJ)/mol by means of NMR spectroscopy. However, this value may also refer to a conformational process, the interconversion of two nonplanar C_2-conformations (Ic) via a planar intermediate. X-Ray data for heptalene could possibly shed further light on this problem, but only the X-ray analyses of 1,2- and 3,8-dicarbmethoxyheptalene have been reported [5,6]. In both compounds, the heptalene system has the conformation shown in Ic. As another approach to the conformational features of heptalene we have determined the structure of bis(tricarbonyliron)heptalene (II) containing the unsubstituted but doubly-complexed heptalene system.

Experimental

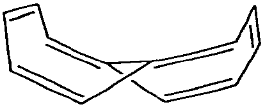
Bis(tricarbonyliron)heptalene was synthesized by Wassen, Zellerhoff and Vogel [7]. Crystals were grown as brown needles (axis [001]) from n-hexane.



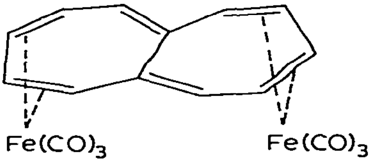
(Ia)



(Ib)



(Ic)



(II)

Crystal data were determined on a STOE four-circle diffractometer by minimizing the orientation matrix for 20 strong reflections. Systematic absences $0k0$ and $h0l$ for $h + l$ at odd indices determined the space group as $P2_1/n$. Crystal data are summarized in Table 1. A single crystal measuring 0.32 × 0.32 × 0.31 mm^3 was selected for data collection of 3275 symmetry-independent reflections $hk0$ to $hk13$ (θ—2θ scan mode, Mo-K_α radiation, graphite monochromator, measuring time: reflex 60 s, undergrounds 2 × 30 s, measuring region θ from 2 to 28° $\hat{=}$ 1/4 of the Ewald sphere).

The data were corrected for background, Lorentz and polarization factors and absorption. Crystal faces for absorption correction are listed in Table 2. 2702 reflections with $|F| > 8\sigma_F$ were taken for structure solution and refinement. The structure was solved using the program SHELX-77 [8]. Scattering factors were taken from ref. 9.

Iron atoms were located by use of a Patterson map, and all other nonhydrogen atoms were found in the subsequent Fourier synthesis. Anisotropic refinement reduced R to 0.085. At this stage hydrogen atoms were geometrically positioned with r(C—H) = 1.08 Å. Four final least squares cycles with isotropic refinement of the hydrogen positions and anisotropic for all other atoms yielded

TABLE 1

CRYSTAL DATA

Molecular formula: $Fe_2C_{18}H_{10}O_6$
M_r = 434 g mol^{-1}
Space group: $P2_1/n$
a = 12.576(1) Å
b = 12.661(2) Å
c = 10.632(2) Å
β = 90.91(3)°
V = 1692.7 $Å^3$
Z = 4
ρ_0 = 1.69 g cm^{-3} (flotation)
ρ_c = 1.70 g cm^{-3}
μ = 16.59 cm^{-1}

TABLE 2

CRYSTAL FACES

Miller indices			d(mm)
−1	1	0	0.154
1	1	0	0.128
1	−1	0	0.211
−1	−1	0	0.154
−1	0	1	0.074
1	0	−1	0.109
1	0	1	0.215
−1	0	−1	0.227

TABLE 3

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

	x/a	*y/b*	*z/c*
Fe(1)	0.90111(2)	0.87619(2)	0.28075(3)
Fe(2)	1.38961(2)	0.93000(3)	0.23053(3)
C(1)	1.0087(2)	−0.1457(2)	0.1282(2)
C(2)	0.9163(2)	−0.0858(2)	0.0935(2)
C(3)	0.8898(2)	0.0039(2)	0.1622(2)
C(4)	0.9564(2)	0.0359(2)	0.2644(2)
C(5)	1.0716(2)	0.0493(2)	0.2617(2)
C(6)	1.2564(2)	0.0338(2)	0.2051(2)
C(7)	1.3296(2)	0.0372(2)	0.1029(2)
C(8)	1.3568(2)	−0.0552(2)	0.0418(2)
C(9)	1.3099(2)	−0.1528(2)	0.0803(2)
C(10)	1.1961(2)	−0.1721(2)	0.0945(2)
C(11)	1.1198(2)	−0.1075(2)	0.1399(2)
C(12)	1.1463(2)	−0.0083(2)	0.2014(2)
C(1')	0.8372(2)	−0.2485(2)	0.2506(2)
O(1')	0.7971(2)	−0.3281(2)	0.2345(2)
C(2')	0.7947(2)	−0.0824(2)	0.3803(2)
O(2')	0.7278(2)	−0.0576(2)	0.4456(2)
C(3')	0.9991(2)	−0.1642(2)	0.3936(2)
O(3')	1.0633(2)	−0.1912(2)	0.4630(2)
C(4')	1.4532(2)	0.0259(2)	0.3308(2)
O(4')	1.4931(2)	0.0857(1)	0.3961(2)
C(5')	1.5135(2)	−0.1389(2)	0.2122(2)
O(5')	1.5926(2)	−0.1814(2)	0.2044(3)
C(6')	1.3316(2)	−0.1511(2)	0.3498(2)
O(6')	1.2954(2)	−0.2037(2)	0.4242(2)
H(C1)	1.008(2)	−0.212(2)	0.100(2)
H(C2)	0.866(2)	−0.117(2)	0.037(2)
H(C3)	0.824(2)	0.036(2)	0.151(2)
H(C4)	0.921(2)	0.084(2)	0.324(2)
H(C5)	1.097(2)	0.107(2)	0.306(2)
H(C6)	1.261(2)	0.097(2)	0.256(2)
H(C7)	1.367(2)	0.101(2)	0.092(2)
H(C8)	1.413(2)	−0.052(2)	−0.018(2)
H(C9)	1.347(2)	−0.212(2)	0.053(2)
H(C10)	1.173(2)	−0.240(2)	0.067(2)

TABLE 3a

THERMAL PARAMETERS U_{ij} USED IN THE FORMULA $T = \exp(-2\pi^2(U_{11}a^{\star 2}h^2 + U_{22}b^{\star 2}k^2 + U_{33}c^{\star 2}l^2 + 2U_{23}b^{\star}c^{\star}kl + 2U_{13}a^{\star}c^{\star}hl + 2U_{12}a^{\star}b^{\star}hk)]$ FOR THE HEAVY ATOMS AND $T = \exp[-U_{11}\sin^2\theta/\lambda^2\, 8\pi^2]$ FOR THE HYDROGEN ATOMS (MULTIPLIED WITH 10^3) AND THEIR ESTIMATED STANDARD DEVIATIONS

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	30.3(0.2)	36.1(0.2)	33.6(0.2)	−3.2(0.1)	5.4(0.1)	0.4(0.1)
Fe(2)	37.7(0.2)	42.1(0.2)	0.9(0.1)	−1.9(0.1)	−0.6(0.1)	0.0(0.1)
C(1)	34(1)	29(1)	34(1)	−3(1)	5(1)	−5(1)
C(2)	32(1)	44(1)	32(1)	5(1)	1(1)	−5(1)
C(3)	33(1)	38(1)	46(1)	9(1)	2(1)	4(1)
C(4)	36(1)	33(1)	46(1)	−3(1)	9(1)	5(1)
C(5)	37(1)	29(1)	44(1)	−2(1)	1(1)	−1(1)
C(6)	35(1)	29(1)	51(1)	2(1)	−2(1)	−2(1)
C(7)	33(1)	48(2)	54(2)	18(1)	−3(1)	−9(1)
C(8)	33(1)	71(2)	38(1)	5(1)	6(1)	−3(1)
C(9)	33(1)	48(2)	40(1)	−9(1)	4(1)	7(1)
C(10)	35(1)	36(1)	34(1)	−2(1)	2(1)	1(1)
C(11)	32(1)	30(1)	27(1)	3(1)	3(1)	1(1)
C(12)	31(1)	27(1)	34(1)	4(1)	−1(1)	−1(1)
C(1′)	39(1)	48(2)	48(1)	4(1)	13(1)	−3(1)
O(1′)	71(1)	51(1)	92(2)	−4(1)	18(1)	−24(1)
C(2′)	47(1)	51(2)	51(2)	5(1)	12(1)	0(1)
O(2′)	68(1)	97(2)	78(2)	−4(1)	41(1)	12(1)
C(3′)	46(1)	57(2)	39(1)	8(1)	8(1)	3(1)
O(3′)	69(1)	115(2)	58(1)	21(1)	−14(1)	21(1)
C(4′)	39(1)	41(1)	57(2)	2(1)	−4(1)	0(1)
O(4′)	69(1)	48(1)	82(2)	−11(1)	−17(1)	−11(1)
C(5′)	42(1)	61(2)	69(2)	−20(1)	−13(1)	6(1)
O(5′)	51(1)	111(2)	138(2)	−52(2)	−21(1)	35(1)
C(6′)	48(1)	44(2)	50(2)	3(1)	−12(1)	0(1)
O(6′)	83(2)	75(2)	73(1)	31(1)	−1(1)	−14(1)
H(C1)	33(6)					
H(C2)	39(6)					
H(C3)	47(7)					
H(C4)	41(7)					
H(C5)	38(6)					
H(C6)	38(6)					
H(C7)	49(7)					
H(C8)	46(7)					
H(C9)	38(6)					
H(C10)	42(7)					

an R value of 0.024. None of the positional parameters shifted more than 0.3 σ in the last cycle. The final parameters are listed in Table 3.

Results and discussion

Heptalene system

The molecular structure of bis(tricarbonyliron)heptalene is indicated in Fig. 1 [10]. The bond lengths (Table 4), the bond and dihedral angles (Table 5) display for the ring system and the iron atoms C_2 symmetry within a maximal deviation of ± 0.01 Å. The two terminal butadiene moieties are *exo* complexed by separate tricarbonyliron groups. In this way a double boat structure is formed with a quite flat internal region (plane IV in Table 7) with a maximal deviation of ±0.07 Å

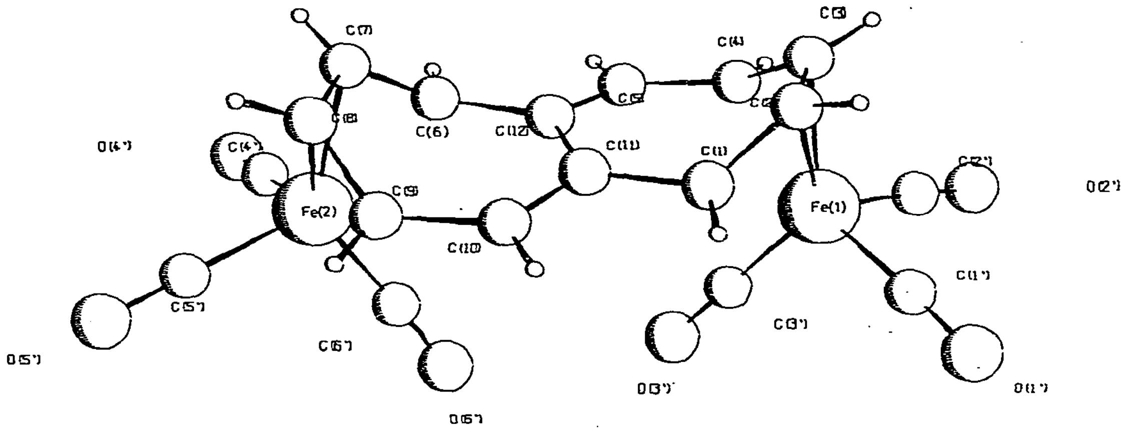


Fig. 1. The structural representation of bis(tricarbonyliron)heptalene with a ball and stick model.

out of plane for C(5) and C(10). The bond angles at the central unit IV and the complexed dienes (II, II') are about 120° while the two angles at atoms lying on the folding lines are about 127°. Between the complexed units a remaining *trans*-butadiene system forms a conjugative bridge with less alternation in the bond lengths compared to butadiene (1.344, 1.467 Å, ref. 11).

Iron—ligand system

The two tricarbonyliron butadiene complexes show similar structural features to those found in other complexes [12—14]. The threefold symmetry of the $Fe(CO)_3$ groups is significantly disturbed by reducing the C(1')(C(4'))—Fe—C(2')(C(5')) angle to about 90° and enlarging the remaining C—Fe—C angles to

TABLE 4

BOND LENGTHS (Å), STANDARD DEVIATION σ = 0.003

C(1)—C(2)	1.432	C(4')—O(4')	1.138
C(2)—C(3)	1.393	C(5')—O(5')	1.135
C(3)—C(4)	1.421	C(6')—O(6')	1.135
C(4)—C(5)	1.458		
		Fe(1)—C(1)	2.147
C(6)—C(7)	1.436	Fe(1)—C(1)	2.060
C(7)—C(8)	1.384	Fe(1)—C(3)	2.054
C(8)—C(9)	1.431	Fe(1)—C(4)	2.147
C(9)—C(10)	1.463		
		Fe(1)—C(1')	1.798
C(1)—C(11)	1.481	Fe(1)—C(2')	1.797
C(10)—C(11)	1.356	Fe(1)—C(3')	1.781
C(5)—C(12)	1.359		
C(6)—C(12)	1.484	Fe(2)—C(6)	2.143
C(11)—C(12)	1.452	Fe(2)—C(7)	2.055
		Fe(2)—C(8)	2.051
C(1')—O(1')	1.138	Fe(2)—C(9)	2.146
C(2')—O(2')	1.143		
C(3')—O(3')	1.138	Fe(2)—C(4')	1.795
		Fe(2)—C(5')	1.799
		Fe(2)—C(6')	1.795

TABLE 5

BOND ANGLES, STANDARD DEVIATION $\sigma = 0.03$ AND DIHEDRAL ANGLES (°) STANDARD DEVIATION $\sigma = 0.1$

Bond angle			
C(11)—C(1)—C(2)	127.54	C(12)—C(6)—C(7)	126.89
C(1)—C(2)—C(3)	119.77	C(6)—C(7)—C(8)	119.75
C(2)—C(3)—C(4)	119.40	C(7)—C(8)—C(9)	119.31
C(3)—C(4)—C(5)	126.28	C(8)—C(9)—C(10)	125.59
C(4)—C(5)—C(12)	129.88	C(9)—C(10)—C(11)	129.49
C(5)—C(12)—C(11)	121.42	C(10)—C(11)—C(12)	121.52
C(1)—C(11)—C(12)	121.98	C(11)—C(12)—C(6)	122.03
C(1)—Fe(1)—C(3′)	91.95	C(6)—Fe(2)—C(6′)	96.57
C(2)—Fe(1)—C(1′)	94.65	C(7)—Fe(2)—C(4′)	95.81
C(3)—Fe(1)—C(2′)	95.00	C(8)—Fe(2)—C(5′)	95.69
C(4)—Fe(1)—C(3′)	95.96	C(9)—Fe(2)—C(6′)	93.22
C(1′)—Fe(1)—C(2′)	91.47	C(4′)—Fe(2)—C(5′)	90.81
C(2′)—Fe(1)—C(3′)	101.58	C(5′)—Fe(2)—C(6′)	99.28
C(3′)—Fe(1)—C(1′)	99.80	C(6′)—Fe(2)—C(4′)	98.60
Dihedral angle			
C(11)—C(1)—C(2)—C(3)	—56.5	C(12)—C(6)—C(7)—C(8)	—57.2
C(1)—C(2)—C(3)—C(4)	1.3	C(6)—C(7)—C(8)—C(9)	1.1
C(2)—C(3)—C(4)—C(5)	50.0	C(7)—C(8)—C(9)—C(10)	51.4
C(3)—C(4)—C(5)—C(12)	—37.6	C(8)—C(9)—C(10)—C(11)	—38.5
C(4)—C(5)—C(12)—C(11)	—9.0	C(9)—C(10)—C(11)—C(12)	—9.5
C(5)—C(12)—C(11)—C(1)	6.3	C(10)—C(11)—C(12)—C(6)	7.2
C(12)—C(11)—C(1)—C(2)	43.9	C(11)—C(12)—C(6)—C(7)	44.0
C(5)—C(12)—C(11)—C(10)	9.0		
C(3)—C(2)—Fe(1)—C(1′)	140.9	C(8)—C(7)—Fe(2)—C(4′)	145.8
C(3)—C(2)—Fe(1)—C(2′)	45.8	C(8)—C(7)—Fe(2)—C(5′)	50.8
C(3)—C(2)—Fe(1)—C(3′)	—112.1	C(8)—C(7)—Fe(2)—C(6′)	—106.3

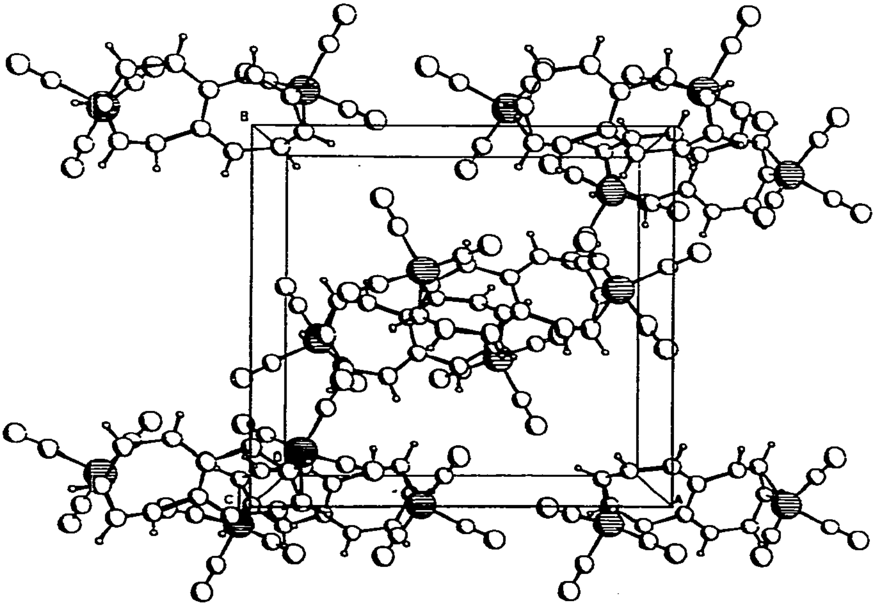


Fig. 2. A view of bis(tricarbonyliron)heptalene down *c* with *a* horizontal and *b* vertical. The unit cell is outlined and the iron atoms are shaded.

100°. C(1′) (C(4′)) and C(2′) (C(5′)) thus form with the midpoints of the complexed butadiene double bonds a plane of a square pyramid, with a s.d. of 0.02 Å, which is almost perpendicular to the butadiene system (87°). The iron atoms are displaced by 0.5 Å towards the apex of the pyramid which is formed by the last carbonyl group tilted by 1° from the normal of the pyramidal base. The two $Fe(CO)_3$ groups are twisted towards each other by 6° (Table 5). This disturbance is not due to strain in the molecule, for the intramolecular distances (Table 6) are not smaller than van der Waals distances. The mutual distortion might be caused by the different environments in the packing.

Crystal packing

The long axes of the molecules are aligned almost in a-direction (Fig. 2). Molecule pairs are formed by the inversion centres through which the molecules are packed, with the uncomplexed parts of the heptalene system facing each other but shifted by half a molecule length in the a-direction (shortest distances (C(12)···C(2) 3.43 Å, C(11)···C(3) 3.47 Å, Table 6 and Fig. 3).

Shortest distances between the so-formed pairs at inversion centres 0, 0, 0 and 1, 0, 1 are 3.10 Å (O(4′)···O(4′)), between the pairs at 0, 0, 0 and 1/2, —1/2,

TABLE 6

SHORTEST INTRA- AND INTERMOLECULAR DISTANCES (Å), STANDARD DEVIATION $\sigma = 0.01$

Fe(1)···Fe(2)	6.21		
O(3′)···O(6′)	2.96		
O(3′)···C(11)	3.68	O(6′)···C(11)	3.91
O(3′)···C(12)	3.78	O(6′)···C(12)	3.89
Carbonyl—carbonyl			
O(5′)···O(3′)	3.05	$(0.5 + x, -0.5 - y, -0.5 + z)$	
O(4′)···O(4′)	3.10	$(3 - x, -y, 1 - z)$	
Ring—ring			
C(12)···H(C2)	2.99	$(2 - x, -y, -z)$	
C(2)	3.43		
C(11)···H(C3)	3.31	$(2 - x, -y, -z)$	
C(3)	3.47		
Ring—carbonyl			
O(4′)···H(C1)	2.57	$(2.5 - x, 0.5 + y, 0.5 - z)$	
C(1)	3.41		
O(3′)···H(C4)	2.65	$(2 - x, -y, 1 - z)$	
C(4)	3.51		
O(6′)···H(C6)	3.24	$(2.5 - x, -0.5 + y, 0.5 - z$	
C(6)		3.65	
O(2′)···H(C10)	2.96	$(-0.5 + x, -0.5 - y, 0.5 + z)$	
C(10)	3.79		
Iron(1)—			
Fe(1)···Fe(1)	6.11	$(1 - x, 1 - y, -z)$	
H(C9)···Fe(1)	3.64	$(0.5 + x, -0.5 - y, -0.5 + z)$	
O(6′)···Fe(1)	4.56	$(0.5 + x, -0.5 - y, 0.5 + z)$	
Iron(2)—			
Fe(1)···Fe(2)	6.16	$(0.5 + x, 0.5 - y, 0.5 + z)$	
Fe(2)···Fe(2)	5.94	$(-x, 1 - y, 1 - z)$	
H(C8)···Fe(2)	3.72	$(3 - x, -y, -z)$	
O(2′)···Fe(2)	4.10	$(2 - x, -y, 1 - z)$	

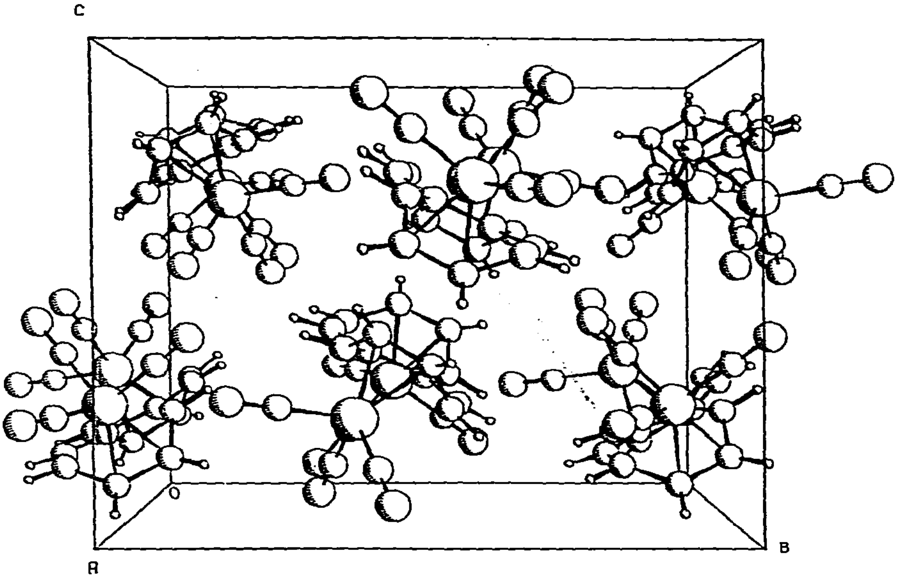


Fig. 3. A view of bis(tricarbonyliron)heptalene down *a* with *b* horizontal and *c* vertical. The unit cell is outlined.

−1/2 3.05 Å (O(5′)···O(3′)) and between 0, 0, 0 and −1/2, 1/2, 1/2 3.41 Å (O(4′)···C(1)). No other short intermolecular distances could be found.

Conclusion

The complexation of heptalene by tricarbonyliron gives the type of complex which is known for cyclohexadiene [12], cycloheptadiene [13] and substituted butadienes [14]. No evidence for van der Waals strain between the tricarbonyliron units is found. The complexed heptalene forms a π-system which is characterized by two complexed butadienes connected via a *trans*-butadiene. But it is questionable whether conclusions concerning the π-structure of the parent hydrocarbon are possible.

Due to the complexation a double boat is formed with structure angles α 6.1° (6.8°) and β 40.2° (41.3°, Table 7). The β angle is 4 times as large as in substituted heptalenes [5,6] while α is reduced by half. These results demonstrate the extreme flexibility of the heptalene system. All perturbations by com-

TABLE 7

LEAST SQUARE PLANES AND STRUCTURE ANGLES (°)

I	C(5)—C(12)—C(11)	I′	C(10)—C(11)—C(12)
II	C(1)—C(2)—C(3)—C(4)	II′	C(6)—C(7)—C(8)—C(9)
III	C(1)—C(4)—C(5)—C(11)	III′	C(6)—C(9)—C(10)—C(12)
IV	C(1)—C(4)—C(5)—C(6)—C(9)—C(10)—C(11)—C(12)		
α_1 = I/III = 6.1°		α_2 = I′/III′ = 6.8°	
β_1 = II/III = 40.2°		β_2 = II′/III′ = 41.3°	

plexation or substitution, possibly even the angle strain in heptalene itself, lead to a double boat structure of the bicyclic system.

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