Acta Cryst. (1984). C**40**, 1718–1721

Structures of Diazapolycyclic Compounds. VIII. 2-Methyl-1,2,3,4-tetrahydrobenzo[*g*]pyridazino[1,2-*b*]phthalazine-6,13-dione (I), $C_{17}H_{16}N_2O_2$, and 1,2,3,4-Tetrahydrobenzo[*g*]pyridazino[1,2-*b*]phthalazine-6,13-dione (II), $C_{16}H_{14}N_2O_2$

By P. T. Beurskens and G. Beurskens

Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands

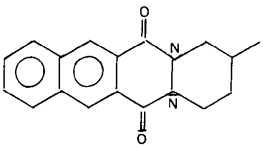
and M. C. Apreda, C. Foces-Foces, F. H. Cano and S. García-Blanco

Departamento de Rayos X, Instituto de Química-Física 'Rocasolano', Serrano 119, Madrid 6, Spain

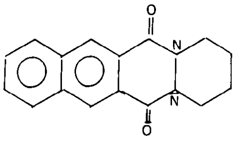
(*Received* 1 *March* 1984; *accepted* 17 *May* 1984)

Abstract. (I): $M_r = 280.33$, triclinic, $P\bar{1}$, $a = 8.0164$ (5), $b = 10.6705$ (8), $c = 17.5227$ (19) Å, $\alpha = 77.08$ (1), $\beta = 101.24$ (1), $\gamma = 99.28$ (1)°, $V = 1421.7$ (2) Å^3, $Z = 4$, $D_x = 1.31$ Mg m^{-3}, Cu $K\alpha$, $\mu = 0.6637$ mm^{-1}, $\lambda = 1.5418$ Å, $F(000) = 592$, room temperature, 4952 unique reflections, $R = 0.058$, $R_w = 0.063$. (II): $M_r = 266.30$, monoclinic, $P2_1$, $a = 14.4453$ (11), $b = 11.1088$ (6), $c = 8.1103$ (3) Å, $\beta = 99.59$ (1)°, $V = 1283.3$ (1) Å^3, $Z = 4$, $D_x = 1.38$ Mg m^{-3}, Cu $K\alpha$, $\mu = 7.087$ cm^{-1}, $F(000) = 560$, room temperature, 2294 unique reflections, $R = 0.041$, $R_w = 0.055$. In compound (I) there is a coupled disorder involving the methyl groups. The pyridazine rings have chair conformations in both compounds. There are no unusual bond distances or angles.

Introduction. The present work on compounds (I) and (II) continues a series of studies on analogues of tetracyclines already reported (Apreda, Foces-Foces, Cano & García-Blanco, 1978, 1982).



(I)



(II)

Experimental. Experimental data and structure solution parameters are summarized in Table 1 together with the refinement procedures. The model for solution of compound (I) was taken from a *MULTAN*78 map (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and used as input to the *DIRDIF* program (Beurskens *et al.*, 1982). At first, *DIRDIF* led to 'chicken-wire' patterns showing the presence of a hexagonal frame in various fragments of the structure. The *DIRDIF* results showed the presence of four parallel molecules in the unit cell, the symmetry-independent molecules being related by a rotation of almost 60°. The structure was solved by carefully

Table 1. *Experimental data and structure refinement procedures*

	(I)	(II)
Crystal shape and size (mm)	Parallelepiped	
	0·43 × 0·23 × 0·10	0·30 × 0·25 × 0·10
Technique, bisecting geometry	Four-circle diffractometer (Philips PW 1100); graphite-monochromated radiation; $\omega/2\theta$ scan mode	
Unit-cell determination	Least-squares fit from	
	64	85
	reflections with $\theta < 45°$	
Total measurements up to $\sin\theta/\lambda$ (Å^{-1})	0·58	0·58
Range of *h,k,l*	$\bar{9}$–9, $\overline{12}$–12, 0–20	$\overline{16}$–16, 0–13, 0–9
Standard reflections	No variation in intensity of	
	015, $0\bar{1}\bar{5}$	120, $\bar{1}\bar{2}0$
Number of reflections measured	4952	2475
Number of independent reflections	4952	2294
Number of observed reflections	2004	2151
Criterion for observed reflections	$I > 2\sigma(I)$	
Absorption correction	None	
Computer programs	*XRAY*70 system (Stewart, Kundell & Baldwin, 1970)	
Solution	*MULTAN*78	Patterson–vector search
	DIRDIF	
Atomic scattering factors	*International Tables for X-ray Crystallography* (1974)	
Refinement method	Six block-diagonal on observed *F*'s	
H atoms	From difference synthesis and geometrical location	From difference synthesis
Parameters refined		
Non-hydrogen atoms	[coordinates, U_{ij} and p.p. [C(21')]]*	(coordinates and U_{ij})
	369	359
H atoms	(coordinates and isotropic temperature factors)	
	80	96
Values for R, R_w	0·058, 0·063	0·041, 0·055
Average Δ/σ in final refinement cycle	0·41	0·62
Weighting scheme	Empirical fit so as to give no trends in $\langle w\Delta^2F\rangle$ *vs* $\langle F_o\rangle$ or $\langle\sin\theta/\lambda\rangle$	
$\Delta\rho_{\max}$ (e Å^{-3})	0·43	0·17
Secondary-extinction correction	None	

* The temperature factors of C(31), C(21), C(21') and C(31') were kept fixed during the refinement. C(21) coordinates also kept fixed.

0108-2701/84/101718-04$01.50

Table 2. *Atomic parameters for compounds* (I) *and* (II)

$U_{eq} = \frac{1}{3}\sum U_{ij}a_i^*a_j^*a_ia_j\cos(a_ia_j)$.

(*a*) Compound (I)

	x	y	z	U_{eq}(Å^2 × 10^3)
C(1)	−0·0625 (6)	0·3458 (7)	0·4196 (4)	90 (2)
C(2)	−0·0491 (7)	0·2688 (6)	0·4991 (4)	97 (2)
C(3)	0·1197 (7)	0·2115 (6)	0·5253 (4)	96 (2)
C(4)	0·2617 (7)	0·3177 (6)	0·5137 (3)	79 (2)
N(5)	0·2458 (4)	0·3928 (3)	0·4321 (2)	61 (1)
C(6)	0·3902 (5)	0·4451 (4)	0·4005 (2)	59 (1)
C(6a)	0·3730 (4)	0·5560 (4)	0·3323 (2)	53 (1)
C(7)	0·5099 (5)	0·6080 (4)	0·2942 (3)	56 (1)
C(7a)	0·4976 (5)	0·7166 (4)	0·2322 (2)	58 (2)
C(8)	0·6363 (6)	0·7715 (5)	0·1903 (3)	73 (2)
C(9)	0·6192 (7)	0·8766 (5)	0·1304 (3)	83 (2)
C(10)	0·4655 (7)	0·9325 (5)	0·1079 (3)	81 (2)
C(11)	0·3300 (6)	0·8823 (4)	0·1457 (3)	68 (2)
C(11a)	0·3410 (5)	0·7727 (4)	0·2090 (2)	56 (1)
C(12)	0·2033 (5)	0·7167 (4)	0·2492 (3)	59 (2)
C(12a)	0·2175 (4)	0·6106 (4)	0·3096 (2)	51 (1)
C(13)	0·0661 (5)	0·5470 (4)	0·3443 (2)	61 (2)
N(14)	0·0871 (4)	0·4431 (4)	0·4051 (2)	62 (1)
O(15)	0·5274 (3)	0·4030 (3)	0·4286 (2)	76 (1)
O(16)	−0·0760 (4)	0·5829 (4)	0·3197 (2)	83 (1)
C(21)	0·1798	0·1811	0·5132	128
C(31)	0·1222 (13)	0·1358 (11)	0·6066 (7)	146
C(1′)	0·2751 (8)	0·1544 (6)	0·2850 (4)	98 (3)
C(2′)	0·4315 (9)	0·1119 (7)	0·3337 (5)	125 (3)
C(3′)	0·5780 (7)	0·1429 (6)	0·2880 (4)	102 (3)
C(4′)	0·5943 (7)	0·2803 (7)	0·2475 (5)	101 (3)
N(5′)	0·4339 (4)	0·3222 (4)	0·1987 (2)	69 (1)
C(6′)	0·4451 (5)	0·4269 (5)	0·1386 (3)	70 (2)
C(6a′)	0·2940 (5)	0·4962 (4)	0·1086 (2)	56 (1)
C(7′)	0·2933 (6)	0·5970 (4)	0·0450 (3)	65 (2)
C(7a′)	0·1529 (5)	0·6680 (4)	0·0180 (3)	59 (2)
C(8′)	0·1493 (7)	0·7750 (5)	−0·0471 (3)	76 (2)
C(9′)	0·0102 (7)	0·8405 (5)	−0·0713 (4)	86 (2)
C(10′)	−0·1319 (7)	0·8040 (5)	−0·0328 (4)	87 (2)
C(11′)	0·1353 (6)	0·7029 (5)	0·0292 (3)	75 (2)
C(11a′)	0·0076 (5)	0·6310 (4)	0·0572 (2)	58 (1)
C(12′)	0·0079 (5)	0·5259 (4)	0·1214 (2)	57 (1)
C(12a′)	0·1484 (5)	0·4589 (4)	0·1476 (2)	53 (1)
C(13′)	0·1446 (5)	0·3464 (4)	0·2132 (2)	59 (1)
N(14′)	0·2880 (4)	0·2846 (3)	0·2370 (2)	64 (1)
O(15′)	0·5794 (4)	0·4644 (4)	0·1115 (2)	98 (2)
O(16′)	0·0195 (4)	0·3059 (3)	0·2462 (2)	80 (1)
C(21′)	0·4122 (13)	−0·0203 (10)	0·3807 (7)	145
C(31′)	0·7121 (106)	0·0577 (50)	0·3118 (45)	97

(*b*) Compound (II)

	x	y	z	U_{eq}(Å^2 × 10^4)
C(1)	0·1515 (3)	0·6274	0·3307 (4)	896 (13)
C(2)	0·1141 (3)	0·6992 (3)	0·1801 (4)	845 (12)
C(3)	0·1183 (3)	0·6261 (3)	0·0240 (4)	777 (11)
C(4)	0·0687 (2)	0·5092 (3)	0·0336 (3)	687 (9)
N(5)	0·1051 (2)	0·4406 (2)	0·1870 (2)	584 (6)
C(6)	0·1034 (2)	0·3195 (2)	0·1822 (3)	576 (7)
C(6a)	0·1124 (2)	0·2549 (2)	0·3423 (3)	521 (7)
C(7)	0·1140 (2)	0·1316 (2)	0·3460 (3)	597 (8)
C(7a)	0·1259 (2)	0·0674 (2)	0·4958 (3)	557 (7)
C(8)	0·1280 (2)	−0·0603 (3)	0·5037 (4)	727 (10)
C(9)	0·1426 (3)	−0·1197 (3)	0·6526 (4)	814 (11)
C(10)	0·1584 (2)	−0·0545 (3)	0·8034 (4)	761 (10)
C(11)	0·1559 (2)	0·0686 (3)	0·8029 (3)	646 (9)
C(11a)	0·1380 (2)	0·1332 (2)	0·6499 (3)	519 (7)
C(12)	0·1326 (2)	0·2588 (2)	0·6440 (3)	522 (7)
C(12a)	0·1193 (1)	0·3200 (2)	0·4943 (2)	480 (6)
C(13)	0·1193 (2)	0·4531 (2)	0·4914 (3)	516 (7)
N(14)	0·1095 (1)	0·5073 (2)	0·3377 (2)	577 (6)
O(15)	0·0944 (2)	0·2661 (2)	0·0482 (2)	840 (8)
O(16)	0·1287 (1)	0·5132 (2)	0·6189 (2)	679 (6)
C(1′)	−0·3842 (2)	1·0396 (2)	0·3289 (4)	695 (10)
C(2′)	−0·3491 (3)	1·1010 (3)	0·1845 (4)	756 (11)
C(3′)	−0·3807 (3)	1·0327 (3)	0·0257 (4)	806 (12)
C(4′)	0·3472 (3)	0·9064 (3)	0·0467 (3)	835 (12)
N(5′)	−0·3781 (2)	0·8460 (2)	0·1906 (2)	644 (7)
C(6′)	−0·3908 (2)	0·7255 (3)	0·1861 (3)	637 (8)
C(6a′)	−0·3842 (2)	0·6619 (2)	0·3465 (3)	530 (7)
C(7′)	−0·3979 (2)	0·5397 (2)	0·3485 (3)	606 (8)
C(7a′)	0·3861 (2)	0·4757 (2)	0·5004 (3)	559 (7)
C(8′)	−0·4026 (2)	0·3501 (2)	0·5067 (4)	666 (9)
C(9′)	−0·3907 (2)	0·2907 (3)	0·6551 (4)	741 (10)
C(10′)	−0·3621 (2)	0·3533 (3)	0·8060 (4)	759 (10)
C(11′)	−0·3455 (2)	0·4751 (3)	0·8051 (3)	703 (9)
C(11a′)	−0·3583 (2)	0·5392 (2)	0·6529 (3)	543 (7)
C(12′)	−0·3453 (2)	0·6653 (2)	0·6479 (3)	552 (7)
C(12a′)	−0·3583 (1)	0·7258 (2)	0·4977 (3)	501 (6)
C(13′)	−0·3503 (2)	0·8583 (2)	0·4955 (3)	543 (7)
N(14′)	−0·3588 (1)	0·9115 (2)	0·3431 (2)	577 (6)
O(15′)	−0·4040 (2)	0·6719 (2)	0·0508 (2)	929 (9)
O(16′)	−0·3384 (2)	0·9183 (2)	0·6234 (2)	713 (7)

evaluating consecutive *DIRDIF* runs in space group *P*1 (ignoring the center of symmetry). The input fragment was kept unchanged. A second molecule was 'selected' and expanded and a third and fourth molecule were accepted and so the structure was solved. The center of symmetry was found and the two independent molecules were shifted accordingly.

For compound (II) the structure was solved by Patterson–vector-search rotation functions (Nordman & Schilling, 1970) followed by *DIRDIF* for the application of direct methods to difference structure factors. The solution of the structure was obtained after expansion of the reflection data for the execution of *DIRDIF* in space group *P*1. At first, *DIRDIF* as well as translation functions in *DIRDIF* Fourier space (Doesburg & Beurskens, 1983) led to 'chicken-wire' patterns and multiple images of the input fragment. This structure was solved in a similar way to compound (I) by consecutive execution of *DIRDIF* in *P*1. At the end, the twofold screw axis was found and the two independent molecules were shifted accordingly.

Discussion. Figs. 1(*a*) and 1(*b*) display the atomic numbering (*ORTEP*, Johnson, 1965). Table 2 shows the coordinates for compounds (I) and (II).* In Table 3 the main geometrical features are displayed.

Compound (I) presents disorder of the methyl groups. Refinement gave values for the population parameters of 0·92 (2) for C(31) and C(21′) and 0·08 (2) for C(21) and C(31′). The distortion parameters for the 'amide groups' (Winkler & Dunitz, 1971) around the N(5)—C(6) and C(13)—N(14) bonds show the usual deformation with respect to sp^2 hybridization ($\chi_N > \chi_C$).

The pyridazine rings have chair conformations in all molecules; both enantiomers are present in one asymmetric unit in compound (II). In compound (II) the diazaquinone rings are more planar than in (I). The attached O atoms O(15), O(16), O(15′) and O(16′) have deviations of −0·101 (3), 0·103 (4), −0·128 (4) and 0·046 (4) Å for compound (I) and 0·050 (3), −0·061 (2), 0·075 (3) and −0·109 (2) Å for compound (II) from the respective least-squares planes.

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39511 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances* (Å) *and angles* (°) *not involving* H *atoms and conformational parameters with e.s.d.'s in parentheses for the non-benzene rings*

	(I*a*)	(I*b*)	(II*a*)	(II*b*)
C(1)–C(2)	1·444 (9)	1·448 (9)	1·483 (4)	1·513 (5)
C(1)–N(14)	1·476 (6)	1·454 (7)	1·470 (3)	1·469 (3)
C(2)–C(3)	1·521 (8)	1·501 (11)	1·514 (5)	1·499 (4)
C(2)–C(21)	1·310 (5)	1·467 (12)	—	—
C(3)–C(4)	1·480 (7)	1·476 (9)	1·491 (5)	1·485 (5)
C(3)–C(31)	1·470 (12)	1·458 (76)	—	—
C(4)–N(5)	1·467 (6)	1·473 (7)	1·479 (3)	1·479 (4)
N(5)–C(6)	1·364 (5)	1·357 (6)	1·346 (3)	1·351 (4)
C(2)–C(1)–N(14)	114·6 (4)	116·9 (5)	115·1 (2)	112·7 (2)
C(1)–C(2)–C(3)	112·1 (5)	111·7 (6)	109·9 (2)	110·1 (3)
C(1)–C(2)–C(21)	115·7 (4)	114·9 (7)	—	—
C(3)–C(2)–C(21)	111·6 (5)	115·1 (8)	—	—
C(2)–C(3)–C(4)	108·5 (5)	110·9 (6)	109·7 (3)	109·4 (3)
C(2)–C(3)–C(31)	108·2 (7)	117·4 (30)	—	—
C(4)–C(3)–C(31)	116·1 (6)	127·3 (27)	—	—
C(3)–C(4)–N(5)	112·9 (4)	114·0 (5)	112·7 (2)	112·6 (3)
C(4)–N(5)–N(14)	113·3 (4)	114·5 (4)	114·4 (2)	114·4 (2)
C(4)–N(5)–C(6)	119·5 (3)	118·1 (4)	119·2 (2)	119·0 (2)
C(6)–N(5)–N(14)	123·0 (3)	122·4 (4)	123·0 (2)	122·5 (2)
N(14)–C(1)–C(2)–C(3)	−50·0 (7)	−46·3 (8)	−52·1 (4)	53·2 (3)
C(1)–C(2)–C(3)–C(4)	53·0 (7)	50·8 (8)	54·6 (4)	−56·9 (4)
C(2)–C(3)–C(4)–N(5)	−55·1 (6)	−52·0 (8)	−54·9 (3)	56·0 (4)
C(3)–C(4)–N(5)–N(14)	54·8 (6)	47·2 (7)	51·6 (3)	−51·0 (3)
C(4)–N(5)–N(14)–C(1)	−48·8 (5)	−40·5 (6)	−46·6 (3)	46·5 (3)
N(5)–N(14)–C(1)–C(2)	47·8 (6)	41·6 (7)	48·1 (3)	−48·0 (3)
		N(5)/N(5′)		
χ_N(°)	−24·4 (5)	−26·1 (5)	−21·9 (3)	24·0 (3)
χ_C(°)	1·3 (5)	1·8 (6)	0·2 (2)	−2·4 (3)
τ(°)	188·8 (4)	187·2 (5)	187·1 (2)	169·4 (2)
$\hat{N}$(°)	118·6 (4)	118·4 (4)	118·9 (2)	118·6 (2)
N(5)–N(14)	1·415 (5)	1·419 (5)	1·422 (3)	1·422 (3)
C(6)–C(6a)	1·484 (5)	1·469 (6)	1·471 (3)	1·470 (3)
C(6)–O(15)	1·226 (5)	1·233 (6)	1·226 (3)	1·235 (3)
C(6a)–C(12a)	1·410 (5)	1·423 (6)	1·370 (4)	1·373 (4)
C(12a)–C(13)	1·463 (5)	1·466 (5)	1·478 (3)	1·478 (4)
C(13)–N(14)	1·362 (5)	1·365 (6)	1·370 (3)	1·357 (3)
C(13)–O(16)	1·227 (5)	1·225 (5)	1·220 (3)	1·221 (3)
N(5)–C(6)–O(15)	120·9 (4)	120·9 (4)	120·6 (2)	120·2 (2)
N(5)–C(6)–C(6a)	116·8 (3)	117·9 (4)	117·6 (2)	117·6 (2)
C(6a)–C(6)–O(15)	122·3 (4)	121·1 (4)	121·8 (2)	122·2 (2)
C(6)–C(6a)–C(12a)	119·4 (3)	119·3 (3)	120·1 (2)	119·7 (2)
C(6a)–C(12a)–C(13)	120·5 (3)	120·3 (4)	119·8 (2)	120·0 (2)
C(12a)–C(13)–O(16)	122·4 (4)	123·1 (4)	122·3 (2)	122·3 (2)
C(12a)–C(13)–N(14)	117·4 (3)	117·3 (4)	117·0 (2)	116·8 (2)
N(14)–C(13)–O(16)	120·2 (4)	119·6 (4)	120·7 (2)	121·0 (2)
N(5)–N(14)–C(13)	122·4 (3)	122·5 (3)	122·4 (2)	123·0 (2)
C(1)–N(14)–C(13)	118·6 (3)	119·0 (4)	117·0 (2)	118·5 (2)
C(1)–N(14)–N(5)	113·5 (4)	115·8 (4)	113·5 (2)	114·7 (2)
C(13)–N(14)–N(5)–C(6)	1·0 (6)	3·7 (6)	4·8 (3)	1·0 (4)
N(14)–N(5)–C(6)–C(6a)	2·9 (6)	−5·0 (6)	3·8 (3)	0·2 (4)
N(5)–C(6)–C(6a)–C(12a)	7·1 (6)	5·4 (6)	2·1 (3)	4·8 (3)
C(6)–C(6a)–C(12a)–C(13)	−9·4 (6)	4·4 (6)	1·2 (3)	8·2 (3)
C(6a)–C(12a)–C(13)–N(14)	7·3 (6)	3·0 (6)	2·0 (3)	7·0 (3)
C(12a)–C(13)–N(14)–N(5)	3·0 (6)	−2·5 (6)	3·6 (3)	2·4 (3)
		N(14)/N(14′)		
	−28·0 (5)	−19·6 (6)	−31·4 (2)	23·4 (3)
	1·2 (5)	0·8 (6)	0·9 (2)	−1·4 (3)
	190·4 (4)	186·9 (4)	191·6 (2)	171·4 (2)
	118·2 (4)	119·1 (4)	117·6 (2)	118·7 (2)

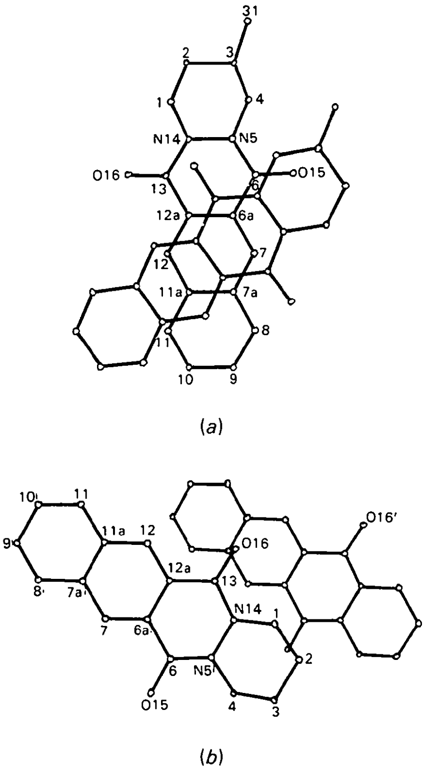


Fig. 1. *ORTEP* drawings for (*a*) compound (I) and (*b*) compound (II), showing the atomic numbering which is assigned to just one molecule.

In compound (I) the angle between the lines through the midpoints of C(9)–C(10) and C(6a)–C(12a) is 54·1 (2)° in each molecule. In compound (II) the equivalent angle is 173·2 (5)°. The ranges of bond distances in the benzene rings are 1·350 (7)–1·427 (6) and 1·358 (4)–1·433 (3) Å for compounds (I) and (II) respectively.

We thank Dr Pilar Navarro and co-workers for providing the material and the Centro de Proceso de Datos del Ministerio de Educación y Ciencia, Madrid, for computer facilities.

References

Apreda, M. C., Foces-Foces, C., Cano, F. H. & García Blanco, S. (1978). *Acta Cryst.* B**34**, 2666–2669.

Apreda, M. C., Foces-Foces, C., Cano, F. H. & García-Blanco, S. (1982). *Acta Cryst.* B**38**, 2834–2838.

Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Van den Hark, Th. E. M., Prick, P. A. J., Noordik, J. H., Beurskens, G., Gould, R. O. & Parthasarathi, V. (1982). *Conformation in Biology*, edited by R. Srinivasan & R. Sarma, pp. 389–406. New York: Adenine Press.

Doesburg, H. M. & Beurskens, P. T. (1983). *Acta Cryst.* A**39**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
NORDMAN, C. E. & SCHILLING, J. W. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 115–123. Copenhagen: Munksgaard.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The *XRAY70* system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
WINKLER, F. K. & DUNITZ, J. D. (1971). *J. Mol. Biol.* **59**, 169–182.

Acta Cryst. (1984). C**40**, 1721–1723

Structure of the Clathrate Inclusion Compound Tetraphenylene–Carbon Tetrachloride (2/1), $2C_{24}H_{16}.CCl_4$

BY HENRY N. C. WONG,* TIEN-YAU LUH AND THOMAS C. W. MAK†

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

(*Received* 18 *April* 1984; *accepted* 30 *May* 1984)

Abstract. $M_r = 762{\cdot}61$, tetragonal, $P4_2/n$, $a = 9{\cdot}930\,(2)$, $c = 18{\cdot}948\,(4)$ Å, $V = 1868{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}356$, D_m (flotation in KI/H_2O) $= 1{\cdot}355$ g cm^{-3}, $F(000) = 788$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 3{\cdot}52$ cm^{-1}, $T = 295$ K, final $R_F = 0{\cdot}097$ and $R_{wF} = 0{\cdot}079$ for 1047 observed reflections. There are no unusual bond distances or angles. The encaged CCl_4 species exhibits orientational disorder within a nearly spherical cavity of free diameter 7·2–7·4 Å.

Introduction. Tetraphenylene (tetrabenzo[*a,c,e,g*]-cyclooctatetraene) (I) was observed to form addition compounds with small solvent molecules such as CH_3COCH_3, $CHCl_3$, CCl_4, C_5H_5N, C_6H_6, and dioxan over four decades ago (Rapson, Shuttleworth & van Niekerk, 1943). These molecular adducts were recently 're-discovered' and shown to be clathrate inclusion compounds of the general formula $2C_{24}H_{16}.G$, where G is a guest species ranging in size from methylene chloride to cyclohexane (Huang & Mak, 1982). Unlike neat tetraphenylene (I), which crystallizes from ethanol in space group $C2/c$ (Irngartinger & Reibel, 1981), the clathrates constitute an isomorphous series belonging to space group $P4_2/n$ with $Z = 2$. X-ray analysis of the $2C_{24}H_{16}.CHCl_3$ clathrate (II) revealed that the host tetraphenylene molecule utilizes crystallographic C_2 symmetry in the construction of the cagework, generating nearly spherical clathration cavities of free diameter‡ 7·0–7·2 Å and site symmetry $\bar{4}$ which accommodate the disordered $CHCl_3$ guest species (Huang & Mak, 1982). A subsequent study of the benzene and cyclohexane clathrates [formulae (III) and (IV), respectively] has established that the tetraphenylene host lattice is capable of adapting itself to the subtle steric requirements of the enclosed guest molecules (Herbstein, Mak, Reisner & Wong, 1984). In order to circumvent the disorder problem, we decided to employ an 'ideal guest species', namely CCl_4 as reported in the present clathrate (V), which fully matches the optimal size and required $\bar{4}$ symmetry of the clathration cavity.

Experimental. Tetraphenylene (I) was prepared by the pyrolysis of biphenylene in the liquid phase (Friedman & Lindow, 1968). Slow evaporation of a solution of (I) in re-distilled carbon tetrachloride at ambient laboratory temperature (295 K) yielded well formed plates of the $2C_{24}H_{16}.CCl_4$ clathrate (V), which gradually turned opaque on exposure to air. A single crystal of (V) was removed from the mother liquor, quickly covered with petroleum jelly, cut to a suitable size (0·4 × 0·4 × 0·3 mm), and sealed in a 0·5 mm

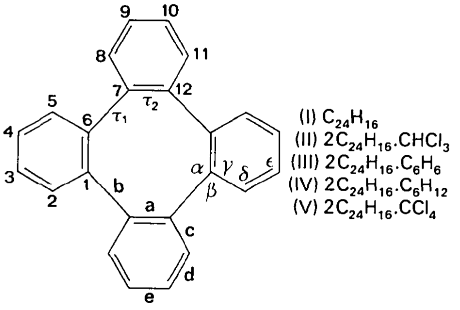


Fig. 1. Structural formula of tetraphenylene (I) showing the numbering system used and labelling of the chemically equivalent bond lengths, bond angles, and torsion angles.

---

* Also known as N. Z. Huang.

† To whom correspondence should be addressed.

‡ As defined by Barrer (1964, p. 318).

0108-2701/84/101721-03$01.50