Polish J. Chem., **75**, 1351–1360 (2001)

CRYSTAL AND MOLECULAR STRUCTURE

X-ray Structural Investigation of 4-Phenyl-, 4-(*o*-Tolyl)- and 4-(2′,4′,6′-Trimethylphenyl)[2.2]paracyclophanes

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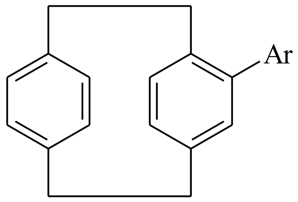
(Received December 28th, 2000; revised manuscript February 26th, 2001)

Crystal structures of 4-phenyl[2.2]paracyclophane (**1**), $C_{22}H_{20}$, monoclinic, $P2_1/c$, a = 14.7168(3), b = 7.8504(1), c = 15.1773(3) Å, β = 118.100(1), Z = 4; 4-(*o*-tolyl)[2.2]paracyclophane (**3**), $C_{23}H_{22}$, monoclinic, *Cc*, a = 11.354(1), b = 22.960(2), c = 7.7156(7) Å, β = 128.824(1), Z = 4; and 4-(2′,4′,6′-trimethylphenyl)[2.2]paracyclophane (**6**), $C_{25}H_{26}$, orthorhombic, *Pbca*, a = 12.892(4), b = 8.091(2), c = 35.895(9) Å, β = 90, Z = 8 have been determined. The interplanar angles between the aryl substituent and the cyclophane ring, to which they are bonded, are 38.0, 50.2 and 56.9° in **1**, **3** and **6**, respectively. For **3**, the methyl group of the substituent points away from the cyclophanyl cavity.

Key words: crystal structure, paracyclophane, aryl[2.2]paracyclophane

Close distances between the aromatic rings of [2.2]paracyclophanes provide strong electronic interactions that are reflected in their spectral properties (particularly ultraviolet spectra). The parent compound, [2.2]paracyclophane has been well characterized spectroscopically and its crystal structure has been reported [1]. Previously crystallographic data for several 4-aryl[2.2]paracyclophanes have been reported [2,3]. The aryl group variation in these compounds includes *p*-tolyl, 2,4,5-trimethylphenyl and 2,6-dimethylphenyl in compounds **2**, **4** and **5**, (Figure 1), respectively. Even bulky substituents at the 4-position did not drastically change the structure from that reported for [2.2]paracyclophane.



	Ar
1	phenyl
2	*p*-tolyl
3	*o*-tolyl
4	2,4,5-trimethylphenyl
5	2,6-dimethylphenyl
6	2,4,6-trimethylphenyl

Figure 1. New and reported 4-aryl[2.2]paracyclophanes.

To better evaluate the structural changes caused by structural variation in 4-aryl[2.2]paracyclophanes, crystal structures have now been determined for compounds with phenyl, (*o*-tolyl) and 2,4,6-trimethylphenyl substituents in **1**, **3** and **6**, respectively. These compounds were prepared by cross-coupling of Grignard reagents [4,5].

EXPERIMENTAL

Transparent, colorless, single crystals of compounds **1**, **3** and **6** were obtained by slow evaporation from ethanol with a few drops of benzene, 95% ethanol and acetonitrile, respectively. Crystallographic, experimental and computational details are presented in Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for compounds **1**, **3** and **6** are given in Tables 2–4, respectively. For **1** and **3**, single crystals were mounted on fibers and transferred to the goniometer. The crystals were cooled to 173 K during data collection by a stream of cold nitrogen gas. Data collection was made on a Siemens SMART diffractometer with a CCD area detector. For data collection and cell refinement Siemens SMART [6] was used. Data reduction was performed with SAINT [7]. The program used to solve, refine and display the structures was SHELXTL [8]. For **6**, the solid-state structure was determined with a Siemens R3m/V diffractometer. Data collection, cell refinement and data reductions were performed with the Siemens Release 3.2 Operating System Software. The program used to solve the structure was SHELXTL-PLUS [9]. For refinement and display of the structure the SHELXTL PC [10] program was employed. For all three structures, the positions of the hydrogen atoms were calculated based on the stereochemistry of the molecule and were refined using the riding model.

Table 1. Crystallographic data and refinement details for **1**, **3** and **6**.

	1	**3**	**6**
Compound	$C_{22}H_{20}$	$C_{23}H_{22}$	$C_{25}H_{26}$
Formula weight	284.38	298.41	326.46
Crystal size/mm	0.15 × 0.18 × 0.20	0.10 × 0.20 × 0.20	0.5 × 0.3 × 0.2
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	*Cc*	*Pbca*
Color/shape	colorless/plate	colorless/fragment	colorless/plate
Unit cell dimensions:			
a/Å	14.7168(3)	11.354(1)	12.892(4)
b/Å	7.8504(1)	22.960(2)	8.091(2)
c/Å	15.1773(3)	7.7156(7)	35.895(9)
$\alpha/\beta/\gamma$/°	90/118.100(1)/90	90/123.84(1)/90	90/90/90
Volume/Å^3	1546.79(5)	1671.0(3)	3744(2)
Z	4	4	8
Density/g/cm^3	1.221	1.186	1.158
Absorption coefficient/mm^{-1}	0.069	0.067	0.065
Temperature/K	173	173	293
Wavelength (MoKα)/ Å	0.71073	0.71073	0.71073
Θ range/°	1.57 to 23.29	1.77 to 23.26	2.27 to 22.55
F(000)	608	640	1408
Reflections collected	5867	3367	2468
Independent reflect.(R_{int})	2220(0.0517)	1799(0.0342)	2468(0.0)
$R1$, $wR2[I > 2\sigma(I)]$	0.0506, 0.1263	0.0431, 0.1101	0.0674, 0.1287
$R1$, $wR2$ [all data]	0.0445, 0.1181	0.0439, 0.1126	0.1665, 0.2126

Table 2. Fractional atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for compound **1**. U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
C1	1974(2)	355(3)	1798(2)	76(1)
C2	998(2)	1683(2)	1110(2)	55(1)
C3	1425(1)	2923(2)	636(1)	41(1)
C4	1957(1)	4419(2)	1122(1)	37(1)
C5	2718(1)	5028(2)	899(1)	39(1)
C6	2948(1)	4248(2)	208(1)	39(1)
C7	2253(1)	3038(2)	–416(1)	44(1)
C8	1515(1)	2385(2)	–192(1)	43(1)
C9	4000(1)	4447(2)	274(1)	47(1)
C10	4773(2)	2977(3)	891(2)	59(1)
C11	4346(1)	1820(2)	1396(1)	46(1)
C12	3786(1)	379(2)	911(1)	50(1)
C13	3044(2)	–269(2)	1134(2)	54(1)
C14	2837(2)	504(2)	1841(2)	54(1)
C15	3550(2)	1694(3)	2465(1)	55(1)
C16	4290(1)	2335(2)	2245(1)	52(1)
C17	1791(1)	5270(2)	1910(1)	39(1)
C18	795(1)	5523(2)	1779(1)	47(1)
C19	627(1)	6376(3)	2487(1)	54(1)
C20	1440(1)	6999(2)	3341(1)	50(1)
C21	2433(1)	6779(2)	3480(1)	46(1)
C22	2606(1)	5918(2)	2779(1)	41(1)

Table 3. Fractional atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for compound **3**. U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
C1	4000(6)	8596(2)	3347(7)	103(2)
C2	3421(4)	9036(1)	4198(5)	57(1)
C3	4515(3)	9240(1)	6401(5)	42(1)
C4	4785(3)	8923(1)	8153(4)	42(1)
C5	6150(3)	8934(1)	9951(4)	45(1)
C6	7235(3)	9264(1)	10105(5)	46(1)
C7	6838(4)	9680(1)	8561(5)	49(1)
C8	5505(3)	9660(1)	6724(5)	46(1)
C9	8766(4)	9104(2)	11614(6)	63(1)
C10	9317(5)	8627(2)	10756(8)	101(2)
C11	8208(4)	8448(2)	8554(6)	70(1)
C12	7913(6)	8791(2)	6876(9)	76(2)
C13	6602(6)	8789(2)	5049(7)	71(1)

Table 3 (continuation)

C14	5530(5)	8438(2)	4831(5)	63(1)
C15	5925(4)	8008(1)	6321(6)	59(1)
C16	7233(4)	8016(2)	8149(6)	63(1)
C17	3682(3)	8539(1)	8065(5)	44(1)
C18	4006(4)	7958(1)	8671(5)	51(1)
C19	3021(4)	7591(2)	8658(5)	60(1)
C20	1714(4)	7806(2)	8056(5)	62(1)
C21	1401(4)	8379(2)	7495(5)	58(1)
C22	2366(4)	8758(1)	7512(5)	50(1)
C23	2005(4)	9396(1)	7072(6)	66(1)

Table 4. Fractional atomic coordinates [×10^4] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for compound **6**. U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
C1	8092(4)	2360(9)	6257(2)	93(2)
C2	8855(4)	1279(7)	6025(2)	72(2)
C3	9868(4)	911(6)	6222(1)	51(1)
C4	10789(4)	1777(6)	6146(1)	46(1)
C5	11505(4)	1939(6)	6437(1)	52(1)
C6	11357(4)	1190(7)	6781(2)	56(1)
C7	10594(5)	–16(7)	6803(2)	64(2)
C8	9847(4)	–124(7)	6529(2)	65(2)
C9	11831(4)	1856(8)	7136(1)	79(2)
C10	11070(5)	2948(8)	7371(2)	85(2)
C11	10055(5)	3311(8)	7176(2)	65(2)
C12	9197(6)	2331(8)	7229(2)	79(2)
C13	8452(5)	2190(8)	6954(2)	77(2)
C14	8547(5)	3004(8)	6617(2)	72(2)
C15	9275(5)	4269(7)	6608(2)	67(2)
C16	10025(5)	4427(7)	6880(2)	65(2)
C17	10990(4)	2486(6)	5765(1)	48(1)
C18	11036(4)	1348(6)	5465(2)	56(2)
C19	11193(4)	1944(8)	5106(2)	69(2)
C20	11319(4)	3599(9)	5031(2)	68(2)
C21	11309(4)	4667(7)	5327(2)	66(2)
C22	11153(4)	4150(6)	5693(2)	55(2)
C23	11201(5)	5461(7)	5993(2)	78(2)
C24	11500(5)	4216(9)	4637(1)	97(2)
C25	10953(5)	–485(6)	5522(2)	82(2)

RESULTS AND DISCUSSION

The solid-state structures of **1**, **3** and **6**, are shown in Figs. 2–4, respectively. The ellipsoids represent 30% probability levels. The bond distances (Table 5) and angles (Table 6) are within the normal range for [2.2]paracyclophane [1]. As observed in earlier work [2,3], the U_{eq} values for C1 and sometimes C10 are larger than those for the other carbons in the [2.2]paracyclophane unit. Thus variation of the 4-aryl substituent does not produce a major change in the paracyclophane geometry.

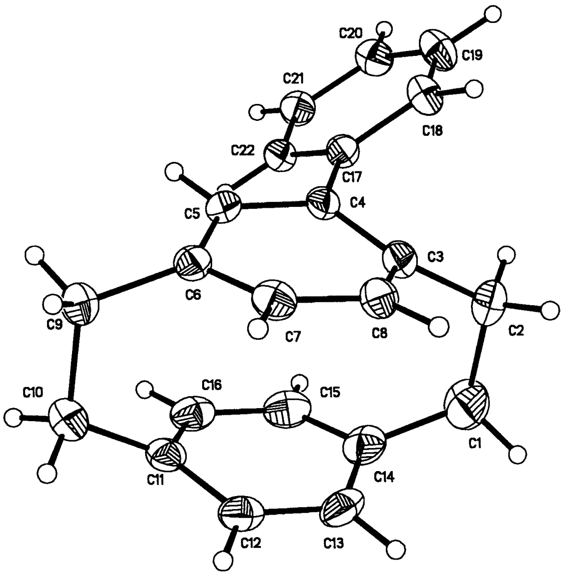


Figure 2. Schematic drawing of compound **1**, showing the numbering scheme.

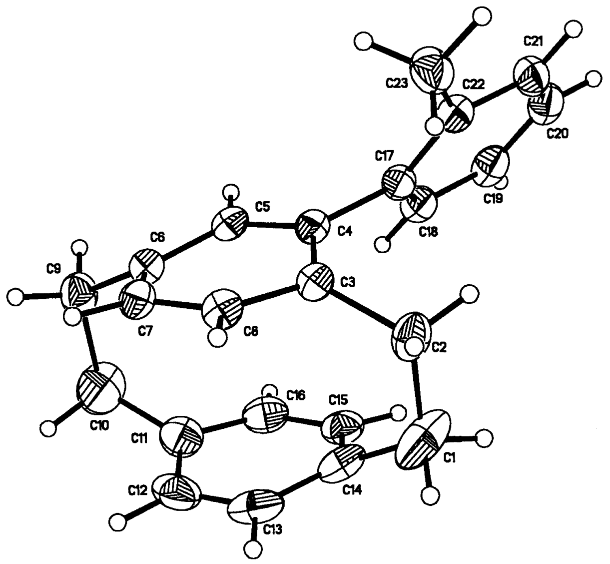


Figure 3. Schematic drawing of compound **3**, showing the numbering scheme.

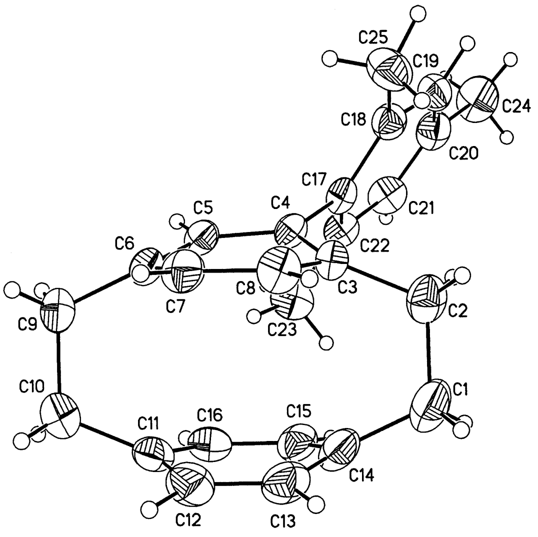


Figure 4. Schematic drawing of compound **6**, showing the numbering scheme.

Table 5. Bond lengths [Å] for compounds **1**, **3** and **6**.

Bond	**1**	**3**	**6**
C(1)–C(14)	1.510(3)	1.498(7)	1.510(7)
C(1)–C(2)	1.548(3)	1.537(6)	1.559(7)
C(2)–C(3)	1.511(2)	1.517(4)	1.514(6)
C(3)–C(8)	1.391(2)	1.395(4)	1.385(6)
C(3)–C(4)	1.412(2)	1.410(4)	1.406(6)
C(4)–C(5)	1.398(2)	1.391(4)	1.401(6)
C(4)–C(17)	1.487(2)	1.503(4)	1.506(6)
C(5)–C(6)	1.387(20)	1.393(4)	1.389(6)
C(6)–C(17)	1.390(2)	1.392(4)	1.387(7)
C(6)–C(9)	1.512(2)	1.504(5)	1.513(7)
C(7)–C(8)	1.380(2)	1.383(4)	1.379(7)
C(9)–C(10)	1.581(3)	1.578(6)	1.565(7)
C(10)–C(11)	1.504(3)	1.503(6)	1.513(7)
C(11)–C(12)	1.389(3)	1.386(6)	1.374(8)
C(11)–C(16)	1.389(3)	1.386(5)	1.392(7)
C(12)–C(13)	1.383(3)	1.366(6)	1.381(8)
C(13)–C(14)	1.387(3)	1.389(6)	1.385(7)
C(14)–C(15)	1.391(3)	1.388(5)	1.389(7)
C(15)–C(16)	1.376(3)	1.365(5)	1.383(7)
C(17)–C(22)	1.396(2)	1.399(4)	1.387(2)
C(17)–C(18)	1.398(2)	1.392(4)	1.417(6)
C(18)–C(19)	1.380(3)	1.396(5)	1.392(7)
C(18)–C(25)			1.501(7)
C(19)–C(20)	1.377(3)	1.376(5)	1.375(8)
C(20)–C(21)	1.386(2)	1.369(5)	1.369(7)
C(20)–C(24)			1.519(7)
C(21)–C(22)	1.382(2)	1.393(5)	1.396(6)
C(22)–C(23)		1.509(4)	1.511(6)

Table 6. Bond angles [°] for compounds **1**, **3** and **6**.

Bond angle	**1**	**3**	**6**
C(14)–C(1)–C(2)	114.1(2)	115.0(3)	113.9(5)
C(3)–C(2)–C(1)	113.7(2)	113.8(3)	113.9(5)
C(8)–C(3)–C(4)	117.3(2)	117.5(3)	118.2(5)
C(8)–C(3)–C(2)	118.2(2)	119.3(3)	118.3(5)
C(4)–C(3)–C(2)	122.7(2)	121.3(3)	122.7(5)
C(5)–C(4)–C(3)	118.0(2)	118.3(3)	117.3(5)
C(5)–C(4)–C(17)	119.7(2)	119.6(3)	122.0(5)
C(3)–C(4)–C(17)	122.2(2)	121.9(3)	120.7(5)
C(6)–C(5)–C(4)	122.7(2)	122.5(3)	122.2(5)
C(5)–C(6)–C(7)	117.0(2)	116.8(3)	117.0(5)
C(5)–C(6)–C(9)	120.7(2)	121.0(3)	122.5(5)
C(7)–C(6)–C(9)	121.2(2)	121.3(3)	119.4(5)
C(8)–C(7)–C(6)	119.8(2)	120.2(3)	120.1(5)
C(7)–C(8)–C(3)	122.1(2)	121.3(3)	121.0(5)
C(6)–C(9)–C(10)	113.1(2)	113.8(3)	113.6(5)
C(11)–C(10)–C(9)	112.7(2)	112.6(3)	113.8(5)
C(12)–C(11)–C(16)	116.7(2)	116.6(4)	117.2(6)
C(12)–C(11)–C(10)	120.5	121.1(4)	121.3(6)
C(16)–C(11)–C(10)	121.2(2)	120.7(4)	120.1(6)
C(13)–C(12)–C(11)	120.6(2)	121.3(4)	120.6(6)
C(12)–C(13)–C(14)	121.0(2)	120.3(4)	121.6(6)
C(13)–C(14)–C(15)	116.7(2)	117.1(4)	123.3(7)
C(13)–C(14)–C(1)	121.5(2)	121.2(4)	119.8(6)
C(15)–C(14)–C(1)	120.5(2)	120.5(4)	121.6(6)
C(16)–C(15)–C(14)	120.7(2)	120.7(4)	121.6(6)
C(15)–C(16)–C(11)	121.2(2)	121.0(3)	119.9(6)
C(22)–C(17)–C(18)	117.4(2)	119.0(3)	119.0(5)
C(22)–C(17)–C(4)	122.0(2)		124.3(5)
C(18)–C(17)–C(4)	120.6(2)	119.3(3)	116.7(5)
C(19)–C(18)–C(17)	121.2(2)	121.0(3)	119.0(5)
C(19)–C(18)–C(25)			118.6(5)
C(17)–C(18)–C(25)			122.4(5)
C(20)–C(19)–C(18)	120.7(2)	119.7(3)	122.3(6)
C(21)–C(20)–C(19)	119.1(2)	119.6(3)	117.6(6)
C(21)–C(20)–C(24)			121.1(6)
C(19)–C(20)–C(24)			121.3(6)
C(20)–C(21)–C(22)	120.5(2)	122.1(4)	122.9(5)
C(17)–C(22)–C(21)			119.1(5)
C(17)–C(22)–C(23)		121.9(3)	123.8(5)
C(21)–C(22)–C(23)		119.3(3)	117.1(5)
C(21)–C(22)–C(17)	121.2(2)	118.7(3)	

A systematic trend is noted as methyl groups are added to the phenyl ring. The torsion angles between the aryl substituent plane and the paracyclophane aryl planes for compounds **1**, **3** and **6** are compared with those reported for **2**, **4** and **5** in Table 7. Thus, the torsion angle of –38.0° observed for the phenyl substituent in **1** increases when a methyl group is introduced in the *para* and *ortho* positions of the phenyl ring in **2** (–42.3°) and **3** (–50.2°) [2]. The larger torsion angle, when the methyl group is in the *ortho* position, is attributed to greater rotation of the aryl substituent plane to reduce interactions with the aromatic rings of the [2.2]paracyclophane unit. In **3**, the methyl group of the substituent points away from the cyclophane cavity. When the 4-aryl substituent is *o*-tolyl in **3** and 2,4,5-trimethylphenyl in **4** [2], the torsion angles are nearly the same, which demonstrates a controlling influence of methyl group in the *ortho* position compared to the *meta* and *para* positions on the phenyl ring. The reported torsion angle of –51.7° in **5** [2] with a 2,6-dimethylphenyl substituent increases to –56.9° in **6** with 2,4,6-trimethylphenyl group. Although the introduction of an additional methyl group in the *para* position would not be expected to increase the bulk of the substituent, it is interesting to note that the addition of a *para* methyl group produces essentially the same increase in torsion angle in going from **5** to **6** as it did in going from **1** to **2**.

Table 7 also lists the distances between directly opposing non-bonded carbon atoms in the two aryl rings of the [2.2]paracyclophane units. Although the C(8)····(13), C(3)····C(14), and C(6)····C(11) distances show minimal changes as the 4-aryl substituent is varied, the C(4)····C(15) distance lengthens when first one and then a second *ortho* methyl group is incorporated.

Table 7. Torsion angles between the planes of the paracyclophane [C(3–8)] and aryl [C(17–22)] rings and selected non-bonded carbon–carbon distances.

Compound	torsion angle [°]	C(4)····C(15) [Å]	C(8)····C(13) [Å]	C(3)····C(14) [Å]	C(6)····C(11) [Å]	Ref.
1	–38.0(1)	3.118(2)	3.031(2)	2.772(2)	2.762(2)	
2	–42.3(4)	3.095(4)	3.110(4)	2.796(4)	2.771(4)	[2]
3	–50.2(1)	3.182(4)	3.002(5)	2.782(4)	2.782(4)	
4	49.1(2)	3.204(2)	2.998(3)	2.790(2)	2.775(2)	[2]
	48.7(2)	3.159(2)	3.028(3)	2.783(2)	2.773(2)	[2]
5	–51.7(3)	3.282(4)	2.990(4)	2.779(4)	2.781(4)	[2]
6	–56.9(5)	3.260(7)	3.012(8)	2.789(8)	2.787(7)	

Packing diagrams of units cells in compounds **1**, **3** and **6** are shown in Figs. 5–7. In the crystal of **6** (Fig. 7), the 2,4,6-trimethylphenyl groups are oriented towards each other to form a channel. This pattern was reported earlier for molecules of **2** [2]. This arrangement is not observed for molecules in the crystals of **1** (Fig. 5), **3** (Fig. 6), **4** [2] or **5** [2].

Complete crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge, CB2 1E2, UK). The deposited structure numbers are: CCDC 161877 for **1**; CCDC 161878 for **3**; and CCDC 161879 for **6**.

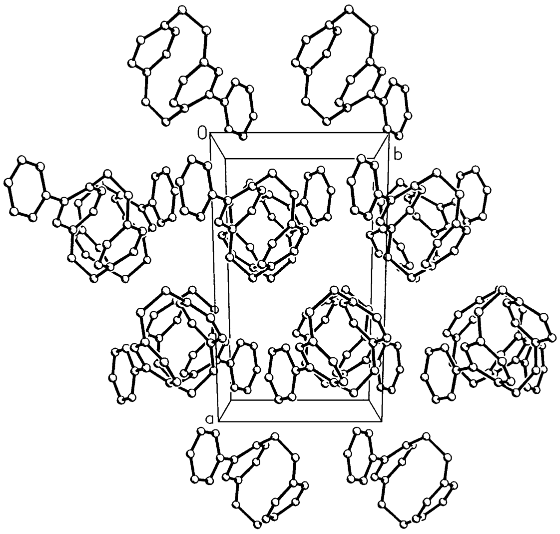


Figure 5. Packing diagram for compound **1**.

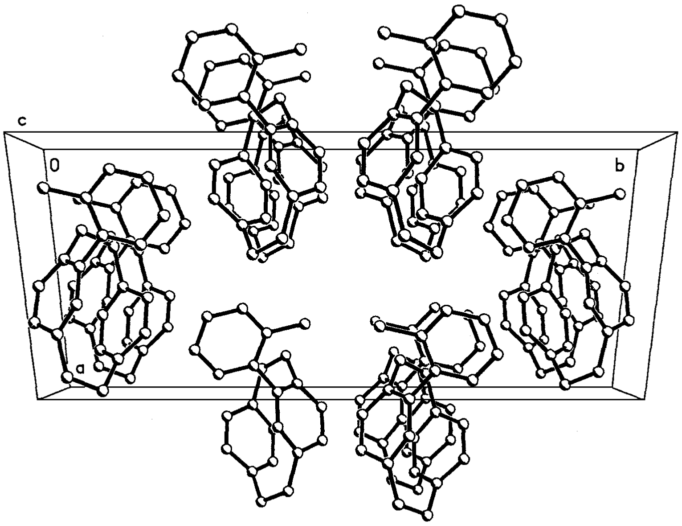


Figure 6. Packing diagram for compound **3**.

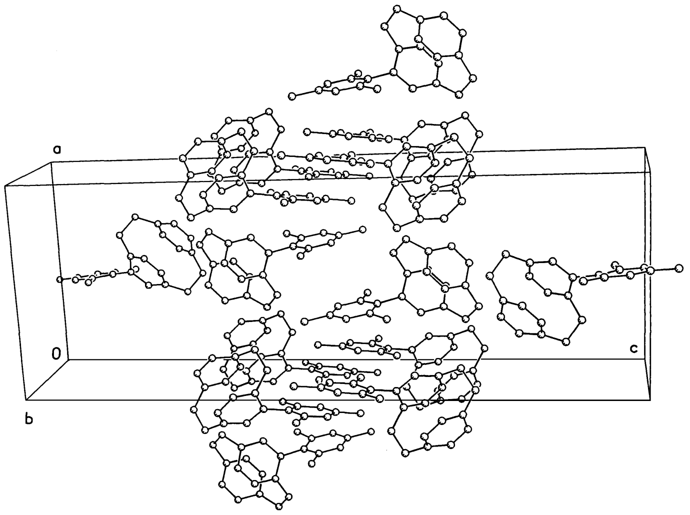


Figure 7. Packing diagram for compound **6**.

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