A Polymorph of 1,2,3,4-Tetraphenyl-naphthalene

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Abstract

The title compound is found to crystallize from solution in space group C2/c with $Z = 12$. Within the asymmetric unit one molecule lies in a general position and a second molecule lies on a crystallographic twofold axis. The crystal packing consists of layers of molecules in general positions alternating with layers of molecules lying on the twofold axes.

Comment

Preparation of the compound 1,2,3,4-tetraphenyl-naphthalene (I) is often used in the undergraduate chemistry laboratory as a textbook example of a Diels–Alder reaction involving a benzyne inter-mediate (Dougherty, Baumgarten, Sweeney & Concepcion, 1977; Fieser & Haddadin, 1965). It also happens to provide an interesting example of polymorphism: the melting point of the compound crystallized from solution is lower than that of the solidified melt. In our laboratory we have observed that crystals grown from solution melt at 475 K, but after cooling and resolidification the compound melts at 481 K (Fisher–Johns melting-point appara-tus). In this report we describe the crystal structure of the polymorph obtained by crystallization from solution.

(I)
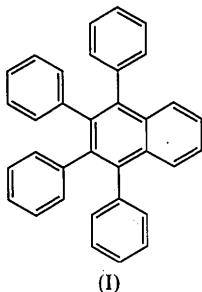
The compound is found to crystallize in space group C2/c with twelve molecules in the unit cell. In the asymmetric unit, one molecule (A) lies in a general position and the other (B) lies on a crystal-lographic twofold axis. The orientation of the phenyl rings in molecule A leads to significant deviation from twofold symmetry, the major deviation being a
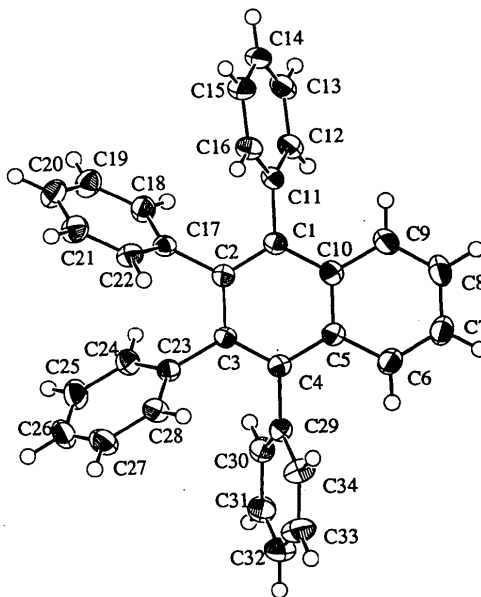

Fig. 1. View of molecule A, showing the atom-numbering scheme. 50% probability displacement ellipsoids are shown for non-H atoms.
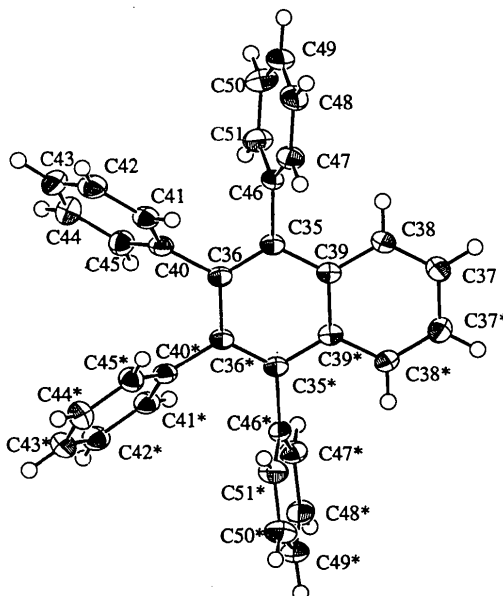

Fig. 2. View of molecule B, showing the atom-numbering scheme. Starred atoms are related to the corresponding unstarred atoms by crystallographic twofold symmetry. 50% probability dis-placement ellipsoids are shown for non-H atoms.

9.0° difference in the torsion angles between the C(1) and C(4) phenyl rings with respect to the naphthalene core. Both molecule A and molecule B are slightly flattened compared with 6-methyl-1,2,3,4-tetraphenylnaphthalene, which has torsion angles of 90, 81, 75 and 78° between the naphthalene core and the pendent phenyl groups (Tao, Silverberg, Rheingold & Heck, 1989). The molecules of 1,2,3,4-tetraphenylnaphthalene lie in distinct layers in the crystal, with layers composed of molecules lying in general positions alternating with layers composed of molecules lying on twofold axes. The naphthalene rings of molecules in adjacent layers lie very nearly perpendicular to each other.

The crystal structure of another tetraphenylnaphthalene, the 1,4,5,8-tetraphenyl isomer, has been described in the literature (Evrard, Piret & Van Meerssche, 1972).
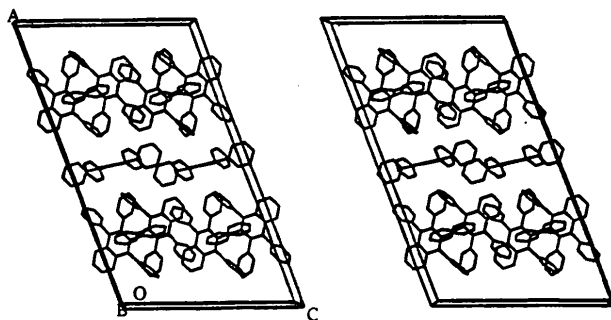

Fig. 3. Stereoview of the molecular packing. H atoms and molecules cut by unit-cell faces have been omitted for clarity.

Experimental

The compound was prepared as described in a laboratory textbook (Pavia, Lampman & Kriz, 1982) and was crystallized from a 1:1 mixture of 95% ethanol and 1,2-dimethoxyethane.

Crystal data

$C_{34}H_{24}$	Cu $K\alpha$ radiation
$M_r = 432.56$	$\lambda = 1.5418$ Å
Monoclinic	Cell parameters from 24
$C2/c$	reflections
$a = 33.057\ (7)$ Å	$\theta = 20.0–25.0°$
$b = 11.842\ (3)$ Å	$\mu = 0.476$ mm^{-1}
$c = 19.777\ (4)$ Å	$T = 173$ K
$\beta = 110.60\ (2)°$	Elongated prism
$V = 7247\ (6)$ Å^3	$0.4 \times 0.1 \times 0.1$ mm
$Z = 12$	Colorless
$D_x = 1.189$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.077$
diffractometer	$\theta_{max} = 70.0°$
$\omega/2\theta$ scans	$h = -32 \rightarrow 40$
Absorption correction:	$k = 0 \rightarrow 14$
none	$l = -24 \rightarrow 22$

11 225 measured reflections
7229 independent reflections
5015 observed reflections
  $[I > 3\sigma(I)]$

3 standard reflections
  frequency: 60 min
  intensity variation:
  insignificant

Refinement

Refinement on F	$\Delta\rho_{max} = 0.20$ e Å^{-3}
$R = 0.043$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
$wR = 0.056$	Extinction correction:
$S = 1.65$	not applied
5015 reflections	Atomic scattering factors
460 parameters	from *International Tables*
H-atom parameters not	*for X-ray Crystallography*
refined	(1974, Vol. IV)
$w = 4F_o^2/\sigma^2(F_o^2)$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	0.30990 (5)	0.1455 (1)	0.35638 (9)	2.20 (5)
C(2)	0.26631 (5)	0.1596 (1)	0.31761 (8)	2.06 (5)
C(3)	0.23478 (5)	0.1326 (1)	0.34967 (8)	2.04 (5)
C(4)	0.24748 (5)	0.0910 (1)	0.41960 (9)	2.13 (5)
C(5)	0.29238 (6)	0.0797 (1)	0.46124 (9)	2.17 (5)
C(6)	0.30684 (6)	0.0369 (2)	0.5330 (1)	2.82 (6)
C(7)	0.34991 (7)	0.0271 (2)	0.5720 (1)	3.50 (7)
C(8)	0.38067 (7)	0.0597 (2)	0.5421 (1)	3.80 (8)
C(9)	0.36821 (6)	0.0994 (2)	0.4727 (1)	3.10 (7)
C(10)	0.32380 (5)	0.1088 (1)	0.42995 (9)	2.26 (5)
C(11)	0.34215 (5)	0.1635 (2)	0.32019 (9)	2.36 (5)
C(12)	0.36494 (6)	0.0713 (2)	0.3072 (1)	2.72 (6)
C(13)	0.39220 (6)	0.0855 (2)	0.2679 (1)	3.03 (7)
C(14)	0.39721 (6)	0.1906 (2)	0.2416 (1)	3.26 (7)
C(15)	0.37548 (6)	0.2829 (2)	0.2554 (1)	3.14 (7)
C(16)	0.34815 (6)	0.2688 (2)	0.2947 (1)	2.65 (6)
C(17)	0.25118 (5)	0.2007 (1)	0.24133 (9)	2.09 (5)
C(18)	0.25633 (6)	0.1370 (2)	0.1859 (1)	2.66 (6)
C(19)	0.24100 (7)	0.1756 (2)	0.1152 (1)	3.21 (7)
C(20)	0.22081 (7)	0.2802 (2)	0.0994 (1)	3.29 (7)
C(21)	0.21598 (7)	0.3442 (2)	0.1541 (1)	3.19 (7)
C(22)	0.23098 (6)	0.3056 (1)	0.2246 (1)	2.62 (6)
C(23)	0.18788 (5)	0.1469 (1)	0.30647 (9)	2.30 (5)
C(24)	0.16812 (6)	0.0825 (2)	0.2445 (1)	2.82 (6)
C(25)	0.12433 (7)	0.0948 (2)	0.2055 (1)	3.50 (7)
C(26)	0.09992 (6)	0.1717 (2)	0.2266 (1)	3.71 (8)
C(27)	0.11933 (6)	0.2380 (2)	0.2873 (1)	3.50 (7)
C(28)	0.16300 (6)	0.2251 (2)	0.3270 (1)	2.86 (6)
C(29)	0.21428 (6)	0.0520 (1)	0.44989 (9)	2.35 (5)
C(30)	0.19133 (6)	-0.0468 (2)	0.4231 (1)	2.84 (6)
C(31)	0.15978 (7)	-0.0834 (2)	0.4492 (1)	3.63 (8)
C(32)	0.15075 (7)	-0.0230 (2)	0.5022 (1)	4.14 (9)
C(33)	0.17348 (8)	0.0740 (2)	0.5291 (1)	3.96 (9)
C(34)	0.20538 (7)	0.1114 (2)	0.5035 (1)	3.25 (7)
C(35)	0.49057 (5)	0.1953 (1)	0.17458 (8)	1.93 (5)
C(36)	0.49498 (5)	0.2962 (1)	0.21145 (7)	1.91 (5)
C(37)	0.49576 (6)	-0.1160 (1)	0.21236 (9)	2.56 (6)
C(38)	0.49170 (5)	-0.0154 (1)	0.17632 (9)	2.18 (5)
C(39)	0.49561 (5)	0.0900 (1)	0.21191 (7)	1.88 (5)
C(40)	0.48758 (5)	0.4051 (1)	0.17101 (8)	2.12 (5)
C(41)	0.51384 (6)	0.4368 (2)	0.13190 (9)	2.55 (6)
C(42)	0.50488 (7)	0.5353 (2)	0.0911 (1)	3.26 (7)
C(43)	0.47007 (8)	0.6017 (2)	0.0881 (1)	3.52 (7)
C(44)	0.44436 (7)	0.5721 (2)	0.1275 (1)	3.42 (7)
C(45)	0.45337 (6)	0.4747 (2)	0.1692 (1)	2.65 (6)
C(46)	0.47884 (6)	0.1913 (1)	0.09412 (8)	2.08 (5)
C(47)	0.50968 (6)	0.1616 (2)	0.0641 (1)	2.71 (6)
C(48)	0.49798 (8)	0.1509 (2)	-0.0103 (1)	3.29 (7)
C(49)	0.45634 (8)	0.1692 (2)	-0.0548 (1)	3.69 (8)
C(50)	0.42564 (8)	0.2006 (2)	-0.0257 (1)	4.00 (8)
C(51)	0.43668 (6)	0.2111 (2)	0.0487 (1)	3.05 (7)

Table 2. Selected geometric parameters (Å, °)

Starred atoms are related to the corresponding unstarred atoms by rotation about a twofold axis.

C(1)—C(2)	1.384 (2)	C(7)—C(8)	1.399 (3)
C(1)—C(10)	1.431 (2)	C(8)—C(9)	1.369 (3)
C(1)—C(11)	1.494 (2)	C(9)—C(10)	1.418 (2)
C(2)—C(3)	1.433 (2)	C(35)—C(36)	1.380 (2)
C(2)—C(17)	1.494 (2)	C(35)—C(39)	1.429 (2)
C(3)—C(4)	1.387 (2)	C(35)—C(46)	1.500 (2)
C(3)—C(23)	1.494 (2)	C(36)—C(36)*	1.442 (3)
C(4)—C(5)	1.428 (2)	C(36)—C(40)	1.492 (2)
C(4)—C(29)	1.496 (2)	C(37)—C(37)*	1.415 (3)
C(5)—C(6)	1.423 (2)	C(37)—C(38)	1.371 (2)
C(5)—C(10)	1.426 (2)	C(38)—C(39)	1.416 (2)
C(6)—C(7)	1.365 (3)	C(39)—C(39)*	1.431 (3)
C(2)—C(1)—C(10)	120.0 (2)	C(7)—C(8)—C(9)	120.8 (2)
C(2)—C(1)—C(11)	119.8 (1)	C(8)—C(9)—C(10)	120.5 (2)
C(10)—C(1)—C(11)	120.2 (1)	C(1)—C(10)—C(5)	119.5 (1)
C(1)—C(2)—C(3)	120.4 (1)	C(1)—C(10)—C(9)	121.7 (2)
C(1)—C(2)—C(17)	120.8 (1)	C(5)—C(10)—C(9)	118.8 (2)
C(3)—C(2)—C(17)	118.8 (1)	C(36)—C(35)—C(39)	120.7 (1)
C(2)—C(3)—C(4)	120.5 (1)	C(36)—C(35)—C(46)	121.9 (1)
C(2)—C(3)—C(23)	119.5 (1)	C(39)—C(35)—C(46)	117.4 (1)
C(4)—C(3)—C(23)	120.0 (1)	C(35)—C(36)—C(36)*	120.07 (9)
C(3)—C(4)—C(5)	119.8 (2)	C(35)—C(36)—C(40)	119.9 (1)
C(3)—C(4)—C(29)	120.1 (1)	C(36)*—C(36)—C(40)	120.02 (8)
C(5)—C(4)—C(29)	120.0 (1)	C(37)*—C(37)—C(38)	119.6 (1)
C(4)—C(5)—C(6)	121.7 (2)	C(37)—C(38)—C(39)	122.2 (2)
C(4)—C(5)—C(10)	119.7 (1)	C(35)—C(39)—C(38)	122.6 (1)
C(6)—C(5)—C(10)	118.6 (2)	C(35)—C(39)—C(39)*	119.19 (8)
C(5)—C(6)—C(7)	120.8 (2)	C(38)—C(39)—C(39)*	118.2 (1)
C(6)—C(7)—C(8)	120.4 (2)		

C(2)—C(1)—C(11)—C(16)	64.9 (2)
C(3)—C(2)—C(17)—C(22)	67.2 (2)
C(4)—C(3)—C(23)—C(28)	65.7 (2)
C(5)—C(4)—C(29)—C(34)	73.9 (2)
C(36)—C(35)—C(46)—C(51)	−76.0 (2)
C(36)*—C(36)—C(40)—C(45)	−62.7 (2)

The rather high value of R_{int} is probably a consequence of the very large fluctuations in the laboratory temperature during data collection. ψ scan results indicated that absorption was negligible. Data collection and cell determination: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction and structure refinement: *TEXSAN* (Molecular Structure Corporation, 1985). Structure solution: *SHELXS*86 (Sheldrick, 1985). H atoms were placed in calculated positions and were not refined. A precautionary check for higher symmetry was conducted using the program *MISSYM* (Le Page, 1987) and none was found. Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1003). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Benzyl 2-[*N*-Benzyl-*N*-(*p*-toluenesulfonyl)-amino]-2-phenylacetate and its α-Amino Acid

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Abstract

The structures of benzyl 2-[*N*-benzyl-*N*-(*p*-toluene-sulfonyl)amino]-2-phenylacetate, $C_{29}H_{27}NO_4S$, (I), and 2-[*N*-benzyl-*N*-(*p*-toluenesulfonyl)amino]-2-phenylacetic acid, $C_{22}H_{21}NO_4S$, (II), have been