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Crystal structure of 1-(*o*-tolyl)-naphthalene

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Abstract

1-(*o*-Tolyl)-naphthalene was obtained in the synthesis of the 1,8-disubstituted analogue. Crystallographic analysis established orthogonal alignment of the ring systems, in agreement with calculations to investigate the existence of rotamers due to restricted rotation.

Introduction

In the absence of steric effects, the energetically preferred conformation of compounds like biphenyl and terphenyl corresponds to a nonplanar and nonorthogonal arrangement of phenyl rings connected through single bonds (Bastiansen and Samdal, 1985; Baraldi and Ponterini, 1985). Experimental evidence (Aikana and Maruyama, 1978; Bart, 1968; Anderson and Hazlehurst, 1980; Ford *et al.*, 1975), consistent with this rule, seems to suggest that it should also apply to naphthyl groups. However, the ring systems in naphthidine and 1,1′-binaphthyl are arranged with dihedral angles of 87 and 102° respectively (Pauptit and Trotter, 1983). It is therefore of interest to establish the dihedral angle in the title compound, which has a phenyl ring connected to the naphthalene residue, and to examine the possibility of separating different rotamers of (1).

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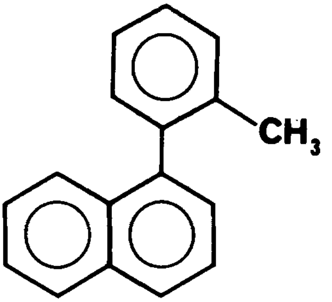

(1)

Preparation

1-*o*-Tolylnaphthalene (1) (mp 71–72 °C) was obtained as the major product in about 30% yield from a reaction designed to synthesize 1,8-di-*o*-tolylnaphthalene by coupling 1,8-diiodonaphthalene with *o*-tolylmagnesium iodide in the presence of nickel acetylacetonate catalyst in a manner used for other instances (Clough *et al.*, 1976; Corriu and Masse, 1972), but reported for this instance (Clough and Roberts, 1976) without disclosing details of the preparation. It was found that 1,8-di-*o*-tolylnaphthalene is so obtained in very low yield, even when the coupling is carried out under forcing conditions (Ibuki *et al.*, 1982), owing to the high degree of crowding which impedes the formation of a collision complex as reaction intermediate. The type of side-reaction that produced (1) has been encountered in related instances (Clough *et al.*, 1972) and is due to Grignard exchange between the *o*-tolylmagnesium iodide and the first-formed 1-iodo-8-*o*-tolynaphthalene.

The major component crystallized from hexane as colorless prisms of 1-*o*-tolylnaphthalene (1) (190 mg), mp 70–72 °C, raised to 71–72 °C on further crystallization (M^+ 218.113; $C_{17}H_{14}$ requires 218.1096), $\delta(CCl_4 + CD_2Cl_2)$ 7.92–7.84 (2H, *m*, ArH), 7.57–7.22 (9H, *m*, ArH), and 2.04 (3H, *s*, CH_3). Crystals suitable for X-ray diffraction analysis were obtained by slow crystallization from hexane.

Measurements routinely involved Kofler micro hot-stage (mp), Varian-MAT CH7 (MS), Bruker WP 80 MHz FT spectrometer (NMR), and Pye Unicam GCD chromatograph (GLC). TLC was on precoated plates of silica gel (Merck F254) or alumina (Merck F254, Type T).

Determination of the structure

A crystal of (1) was sealed into a Lindemann tube and mounted on an Enraf-Nonius CAD4 diffractometer, equipped with an incident-beam graphite-

Table 1. Crystal data and details of the structure analysis.

Formula	$C_{17}H_{14}$
M_r	218.30
Space Group	$Iba2$
a (Å)	15.334(2)
b (Å)	21.330(3)
c (Å)	7.596(8)
U (Å^3)	2484.5
Z	8
D_c (g cm^{-3})	1.17
F(000)	928
μ(Mo $K\alpha$) (cm^{-1})	0.33
Crystal size	0.5 × 0.3 × 0.2 mm
Scan range (deg)	$3 < \theta < 30$
Scan mode	ω–2θ
h	0 to 10
k	0 to 30
l	0 to 21
Observed data	1076
Cut-off	$F < 2\sigma(F)$
Parameters	154
Maximum shift/esd	0.02
Residual density (e A^{-3})	0.27
Conventional R	0.080
Weighting	Unit weights

crystal monochromator, using Mo $K\alpha$ radiation at room temperature. Accurate cell constants were obtained from refinement of the accurately measured θ values of 25 high-angle reflections. Intensity data were collected under conditions specified in Table 1, which also summarizes crystal data and details of the structure refinement. Data reduction consisted of correction for background and *Lp* factors only. The structure was solved by the direct methods procedure of the program SHELXS 86 (Sheldrick, 1985), and refined by full-matrix least squares using the program SHELX 76 (Sheldrick, 1978). Some hydrogen atoms that could not be placed from difference Fourier analyses were placed in geometrically calculated positions and refined in the riding mode. The refined atomic coordinates in Table 2 are listed according to the numbering scheme of Fig. 1, which represents the refined molecular structure. Bond parameters and structure factor tables have been deposited as supplementary material.

Discussion

The *o*-tolyl group has virtually no effect on the geometry of the naphthalene nucleus and sits at right angles to it. As in the structure of naphthalene

Table 2. Fractional coordinates (× 10^4) and equivalent isotropic temperature factors (Å^2, × 10^3) for nonhydrogen atoms.

	x	*y*	*z*	*U*(eq)
C(1)	2037(4)	3338(3)	2473(2)	46(1)
C(2)	1944(5)	2711(3)	2798(14)	59(2)
C(3)	1351(5)	2339(4)	1808(15)	67(2)
C(4)	873(5)	2600(4)	493(15)	62(2)
C(5)	520(5)	4151(4)	−1569(14)	67(2)
C(6)	1091(5)	4533(4)	−611(14)	63(2)
C(7)	1600(5)	4268(3)	689(13)	49(2)
C(8)	962(4)	3234(3)	83(13)	50(2)
C(9)	448(5)	3528(4)	−1238(13)	64(2)
C(10)	1544(4)	3619(3)	1084(12)	41(1)
C(11)	2657(4)	3722(3)	3526(13)	50(2)
C(12)	3487(5)	3862(4)	2952(14)	56(2)
C(13)	4045(5)	4226(4)	3991(13)	66(2)
C(14)	3759(7)	4460(4)	5597(16)	79(3)
C(15)	2937(7)	4324(4)	6201(14)	76(2)
C(16)	2380(5)	3956(4)	5178(14)	66(2)
C(17)	3813(5)	3599(5)	1234(15)	84(3)

itself (Brock and Dunitz, 1982), the bonds in the meta position with respect to the common bond are uniformly shorter than all the others, with an average value of 1.366(5) Å, compared to an average of 1.417(4) Å for the seven remaining naphthalene bonds.

Although the variation in bond angle is much smaller, the same trends as in naphthalene are observed. The six bonds in the phenyl ring do not differ significantly among themselves and have an average length of 1.392(4) Å (Table 3). The two bond angles between the phenyl ring and the connecting bond are 118.6(6) and 122.6(6)° respectively, with the larger of the two on the side of the methyl substituent. The only special feature of the structure, therefore, is this 4° tilt of the *o*-tolyl group with respect to the naphthalene plane, to allow for the steric demands of the methyl group.

The regular 90° dihedral angle observed here is in contrast to intermediate angles that would allow the separate existence of rotamers, observed before for related compounds. To establish which form is preferred energetically, the stereodynamics of (1) was investigated by molecular mechanics, using the computer program of Boyd (1968) suitably modified to systematically explore molecular steric energy as a function of independent rotation about two selected bonds. Full details of the procedure were described before (Allenspach-Wasser *et al.*, 1987). It consists of forced rotation in preselected steps, with energy

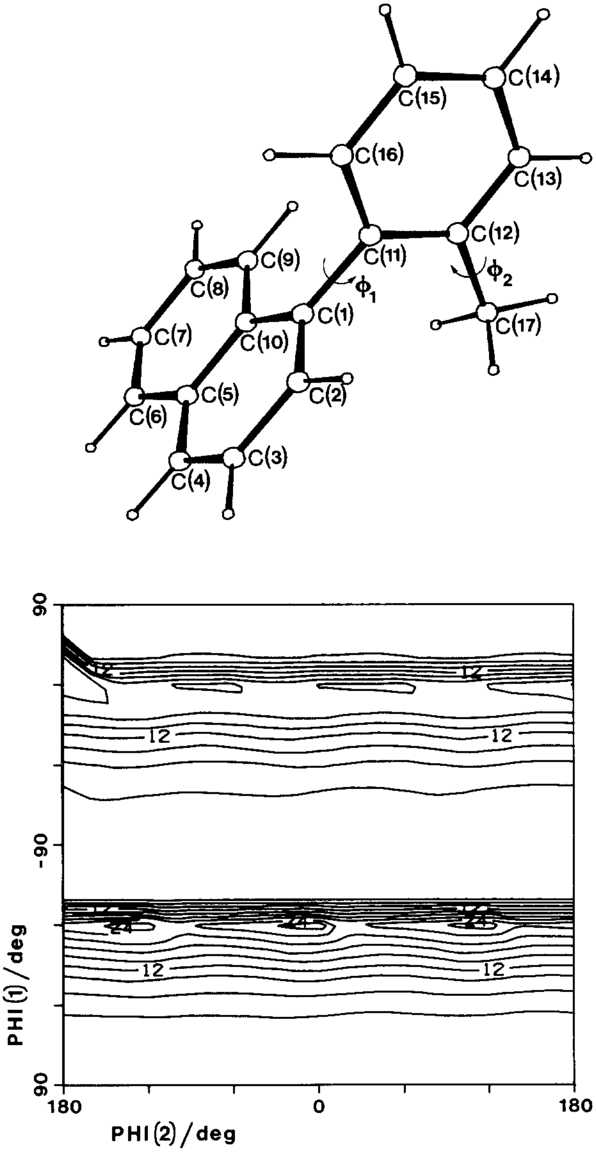

Fig. 1. Atomic numbering scheme and contour map of the potential steric energy as a function of the independent rotation of the tolyl (ϕ_1) and methyl (ϕ_2) groups. Contours are drawn at intervals of 3 kcal/mole.

Table 3. Bond lengths (Å) and angles (deg) of OR44.

C(1)-C(2)	1.367(9)	C(1)-C(10)	1.430(9)
C(1)-C(11)	1.488(9)	C(2)-C(3)	1.422(10)
C(3)-C(4)	1.359(11)	C(4)-C(9)	1.393(10)
C(5)-C(6)	1.356(10)	C(5)-C(9)	1.423(10)
C(6)-C(7)	1.399(11)	C(7)-C(8)	1.380(10)
C(8)-C(10)	1.420(8)	C(9)-C(10)	1.432(8)
C(11)-C(12)	1.378(9)	C(11)-C(16)	1.415(10)
C(12)-C(13)	1.399(10)	C(12)-C(17)	1.506(11)
C(13)-C(14)	1.390(12)	C(14)-C(15)	1.374(12)
C(15)-C(16)	1.397(11)		
C(2)-C(1)-C(10)	119.2(6)	C(2)-C(1)-C(11)	120.6(6)
C(10)-C(1)-C(11)	120.2(6)	C(1)-C(2)-C(3)	121.2(7)
C(2)-C(3)-C(4)	120.3(7)	C(3)-C(4)-C(9)	120.6(7)
C(6)-C(5)-C(9)	121.2(7)	C(5)-C(6)-C(7)	121.7(7)
C(6)-C(7)-C(8)	119.2(7)	C(7)-C(8)-C(10)	121.0(7)
C(4)-C(9)-C(5)	122.1(7)	C(4)-C(9)-C(10)	120.0(7)
C(5)-C(9)-C(10)	117.8(6)	C(1)-C(10)-C(8)	122.2(6)
C(1)-C(10)-C(9)	118.7(6)	C(8)-C(10)-C(9)	119.1(6)
C(1)-C(11)-C(12)	122.6(6)	C(1)-C(11)-C(16)	118.6(7)
C(12)-C(11)-C(16)	118.8(7)	C(11)-C(12)-C(13)	120.4(7)
C(11)-C(12)-C(17)	120.0(7)	C(13)-C(12)-C(17)	119.5(7)
C(12)-C(13)-C(14)	120.2(8)	C(13)-C(14)-C(15)	120.4(8)
C(14)-C(15)-C(16)	119.6(8)	C(11)-C(16)-C(15)	120.6(8)

minimization after each elementary rotation. Since only qualitative details of the potential energy surface are required to identify possible rotamers, convergence criteria need not be very stringent, and random fluctuations from expected geometry occur routinely.

The contour map shown in Fig. 1 represents the potential steric energy as a function of the independent rotation of the *o*-tolyl and methyl groups respectively. The expected three-fold symmetry with respect to the rotation of the methyl group is clearly evident. It has little effect on the total steric energy. Minimum energy situations occur at $\phi(1) = \pm 90^\circ$, which represents orthogonal alignment of the aromatic planes, in full agreement with the structure analysis. One finds that, whereas about 88 kJ mol^{-1} is required to force the methyl group across the naphthalene ring, only 76 kJ mol^{-1} is needed for the *ortho*-hydrogen side to pass over.

Molecular mechanics predicts a orthogonal alignment as preferred by the isolated molecule, and hence the observed arrangement is not due to intermolecular interactions. The stereoscopic packing diagram shown in Fig. 2 does not suggest any intermolecular effects.

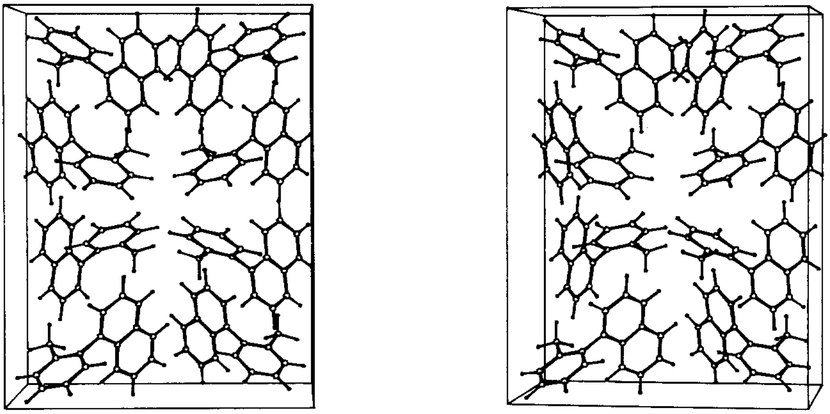

Fig. 2. Stereoscopic packing diagram showing the contents of one unit cell.

References

Aikawa, S., and Maruyama, Y. (1978) *Acta Crystallogr. B* **34,** 2901.

Allenspach-Wasser, C. E., Boeyens, J. C. A., and Denner, L. (1987) *S. Afr. J. Chem.* **40,** 47.

Anderson, J. E., and Hazlehurst, C. J. (1980) *J. Chem. Soc. Chem. Commun.*, 1188.

Baraldi, I., Ponterini, G. (1985) *J. Mol. Struct.* **122,** 287.

Bart, J. C. J. (1968) *Acta Crystallogr. B* **24,** 1277.

Bastiansen, O., and Samdal, S. (1985) *J. Mol. Struct.* **128,** 115.

Boyd, R. H. (1968) *J. Chem. Phys.* **49,** 2574.

Brock, C. P., and Dunitz, J. D. (1982) *Acta Crystallogr. B* **38,** 2218.

Corriu, R. J. P., and Masse, J. P. (1972) *J. Chem. Soc. Chem. Commun.*, 144.

Clough, R. L., and Roberts, J. D. (1976) *J. Am. Chem. Soc.* **98,** 1018.

Clough, R. L., Mison, P., and Roberts, J. D. (1976) *J. Org. Chem.* **41,** 2252.

Ford, W. T., Thompson, T. B., Snoble, K. A. J., and Timko, J. M. (1975) *J. Am. Chem. Soc.* **97,** 95.

Ibuki, E., Ozasa, S., Fujioka, Y., and Mizutani, H. (1982) *Bull. Chem. Soc. Jpn.* **55,** 845.

Pauptit, R. A., and Trotter, J. (1983) *Can. J. Chem.* **61,** 69 (1983).

Sheldrick, G. M. (1978) In *Computing in Crystallography*, H. Schenk, R. Olthof-Hazelkamp, H. van Koningsveld, and G. C. Bassi, eds. (Delft University Press, The Netherlands).

Sheldrick, G. M. (1985) In *Crystallographic Computing* 3′, G. M. Sheldrick, C. Krüger, and R. Goddard, eds. (Oxford University Press, Oxford, England).

Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 60548 (6 pages).