

S(1')	0.4994 (1)	0.4893 (1)	-0.2602 (1)	56 (1)
O(1')	0.3478 (3)	0.8170 (3)	0.0228 (3)	55 (1)
C(2')	0.2532 (4)	0.7425 (4)	-0.0523 (4)	50 (2)
C(3')	0.3106 (4)	0.6526 (4)	-0.1154 (4)	49 (2)
C(3'a)	0.4505 (4)	0.6700 (3)	-0.0788 (4)	42 (1)
C(4')	0.5480 (4)	0.5909 (4)	-0.1306 (4)	46 (2)
N(5')	0.6725 (3)	0.6013 (3)	-0.0751 (4)	50 (1)
C(6')	0.7336 (4)	0.6711 (4)	0.0467 (4)	51 (2)
C(7')	0.7127 (4)	0.8105 (4)	0.0450 (4)	47 (2)
C(8')	0.5811 (4)	0.8399 (4)	0.0830 (5)	56 (2)
C(8'a)	0.4678 (4)	0.7712 (4)	0.0041 (4)	49 (2)
C(9')	0.1153 (4)	0.7752 (4)	-0.0444 (5)	67 (2)
C(10')	0.8186 (4)	0.8701 (4)	0.1525 (5)	61 (2)
C(11')	0.7223 (5)	0.8607 (4)	-0.0949 (5)	64 (2)

Table 2. Geometric parameters (Å, °)

S(1)—C(4)	1.683 (4)	O(1)—C(2)	1.383 (5)
O(1)—C(8a)	1.372 (5)	C(2)—C(3)	1.331 (6)
C(2)—C(9)	1.474 (7)	C(3)—C(3a)	1.445 (6)
C(3a)—C(4)	1.453 (6)	C(3a)—C(8a)	1.359 (5)
C(4)—N(5)	1.317 (5)	N(5)—C(6)	1.450 (6)
C(6)—C(7)	1.531 (6)	C(7)—C(8)	1.524 (6)
C(7)—C(10)	1.526 (6)	C(7)—C(11)	1.505 (7)
C(8)—C(8a)	1.473 (6)	S(1')—C(4')	1.680 (4)
O(1')—C(2')	1.375 (5)	O(1')—C(8'a)	1.376 (5)
C(2')—C(3')	1.335 (6)	C(2')—C(9')	1.485 (6)
C(3')—C(3'a)	1.443 (5)	C(3'a)—C(4')	1.472 (6)
C(3'a)—C(8'a)	1.345 (5)	C(4')—N(5')	1.316 (5)
N(5')—C(6')	1.457 (5)	C(6')—C(7')	1.529 (6)
C(7')—C(8')	1.506 (6)	C(7')—C(10')	1.524 (6)
C(7')—C(11')	1.530 (6)	C(8')—C(8'a)	1.485 (6)
C(2)—O(1)—C(8a)	107.6 (3)	O(1)—C(2)—C(3)	109.4 (4)
O(1)—C(2)—C(9)	115.7 (4)	C(3)—C(2)—C(9)	134.8 (4)
C(2)—C(3)—C(3a)	107.6 (4)	C(3)—C(3a)—C(4)	124.6 (3)
C(3)—C(3a)—C(8a)	106.1 (4)	C(4)—C(3a)—C(8a)	129.3 (4)
S(1)—C(4)—C(3a)	120.5 (3)	S(1)—C(4)—N(5)	120.6 (3)
C(3a)—C(4)—N(5)	118.9 (4)	C(4)—N(5)—C(6)	129.2 (4)
N(5)—C(6)—C(7)	115.2 (3)	C(6)—C(7)—C(8)	109.7 (4)
C(6)—C(7)—C(10)	107.3 (3)	C(8)—C(7)—C(10)	107.3 (4)
C(6)—C(7)—C(11)	111.1 (4)	C(8)—C(7)—C(11)	111.4 (4)
C(10)—C(7)—C(11)	109.8 (4)	C(7)—C(8)—C(8a)	115.8 (4)
O(1)—C(8a)—C(3a)	109.3 (3)	O(1)—C(8a)—C(8)	113.3 (3)
C(3a)—C(8a)—C(8)	137.4 (4)	C(2')—O(1')—C(8'a)	107.4 (3)
O(1')—C(2')—C(3')	109.4 (3)	O(1')—C(2')—C(9')	116.1 (4)
C(2')—C(3')—C(3'a)	134.5 (4)	C(2')—C(3')—C(3'a)	107.4 (3)
C(3')—C(3'a)—C(4')	123.9 (3)	C(3')—C(3'a)—C(8'a)	106.2 (4)
C(4')—C(3'a)—C(8'a)	129.8 (4)	S(1')—C(4')—C(3'a)	119.7 (3)
S(1')—C(4')—N(5')	120.8 (3)	C(3'a)—C(4')—N(5')	119.4 (4)
C(4')—N(5')—C(6')	129.8 (4)	N(5')—C(6')—C(7')	116.2 (3)
C(6')—C(7')—C(8')	109.0 (4)	C(6')—C(7')—C(10')	108.1 (3)
C(8')—C(7')—C(10')	108.5 (4)	C(6')—C(7')—C(11')	111.2 (4)
C(8')—C(7')—C(11')	110.8 (3)	C(10')—C(7')—C(11')	109.2 (4)
C(7')—C(8')—C(8'a)	116.0 (4)	O(1')—C(8'a)—C(3'a)	109.6 (3)
O(1')—C(8'a)—C(8')	114.0 (3)	C(3'a)—C(8'a)—C(8')	136.4 (4)

Data were corrected for Lorentz-polarization effects. The structure was solved by direct methods (*SHELXTL*; Sheldrick, 1985). The H-atom positions in the CH, CH₂ and CH₃ groups were calculated. Non-H atoms were refined anisotropically. The H atoms were assigned the fixed isotropic displacement parameter 0.060 Å² and coordinates of H atoms bonded to N were refined.

We are greatly indebted to Mr R. A. Toscano and Mrs Cynthia E. Lesh for technical assistance.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71115 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1036]

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- Boessenkool, I. K. & Boeyens, J. C. A. (1980). *J. Crystallogr. Spectrosc. Res.* **10**, 11–18.
- Sheldrick, G. M. (1985). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Revision 5.1. Univ. of Göttingen, Germany.
- Weiss, M. J., Gibb, G. J., Poletto, J. F. & Remers, W. A. (1973). US Patent 3 758 501.

Acta Cryst. (1993). **C49**, 1638–1640

Structure of a 2-Arylquinoline Dimer, a Compound with a New Ring System

HERMAN L. AMMON

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

THEODORE L. REID†

Department of Chemistry, American University, Washington, DC 20016, USA

(Received 2 June 1992; accepted 8 February 1993)

Abstract

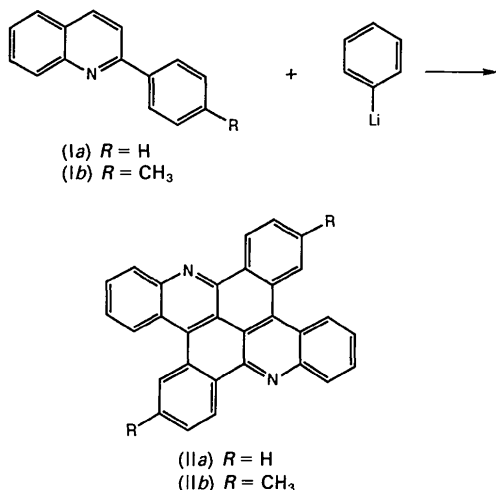
The title compound, 6,15-dimethyltribenzo-*[c,f,j]*naphtho[1,2,3,4-*lmn*][2,7]phenanthroline, was obtained in low yield from the reaction of 2-(4-methylphenyl)quinoline and various aryl-lithiums. The compound is a 'dimer' in which two phenylquinoline units are joined by three bonds; the dimer has exact twofold symmetry. Non-bonded interactions produce substantial out-of-plane distortions. Bond lengths between the two phenylquinoline halves suggest that the two phenylquinoline π -electron systems are more-or-less undisturbed and linked by single bonds. Molecular-mechanics optimizations of models with inversion ($\bar{1}$) and twofold symmetry suggest that the latter conformation is the more stable of the two to a slight extent.

Comment

The reactions of certain 2-arylquinolines with aryl-lithiums (*e.g.* aryl = phenyl, 2-methylphenyl, 4-methylphenyl, 2,4,6-trimethylphenyl) give, in low yield, 'dimeric' products with molecular weights that are equal to twice that of the starting arylquinoline

† On leave from the National Science Foundation.

minus 6. ^{13}C NMR spectra suggest that the products have substantial molecular symmetry; the product spectra show only a few more resonances than the starting arylquinoline system. In this paper, we report the crystal and molecular structure of the product (IIb) obtained from 2-(4-methyl)quinoline (Ib). (IIa) has been isolated and spectroscopically characterized, but crystals suitable for a crystallographic analysis have not been obtained.



An ORTEP drawing of the molecule is shown in Fig. 1; the molecule occupies a twofold crystallographic axis. The 'dimer' can be envisioned as two phenylquinoline units joined by three single bonds, which explains the loss of 6 a.m.u. (the formation of three C—C bonds eliminates six H atoms). Although the molecule can be regarded as a polynuclear aromatic, bond lengths such as C3—C3' = 1.444 (3), C4—C10' = 1.464 (2) and C2—C9 = 1.463 (2) Å suggest that a more realistic view is one in which the two arylquinoline π -electron systems are essentially undisturbed and linked by single bonds. Non-bonded interactions between C5 and C11' [distance = 3.061 (2) Å; see Fig. 2] are relieved by an overall twist which lifts the C9—C15 methylphenyl nucleus above the opposing quinoline. The largest deviation of an atom from the mean plane of the dimer is 1.29 Å (C6). One could envision the formation of a dimer with the observed twofold symmetry, in which the two methylphenyl rings are positioned on one side of the mean plane of the molecule with the two quinolines on the other, or a dimer with inversion ($\bar{1}$) symmetry. In the $\bar{1}$ dimer the methylphenyls are on opposite sides of the mean plane as are the quinolines. Geometry optimization of dimeric models with $\bar{1}$ and twofold symmetry with the molecular-mechanics force field in *MACROMODEL* (Still, 1990) revealed that the latter is the more stable conformation by 0.4 kJ mol $^{-1}$.

A search of the January 1993 version of the Cambridge Structural Database for crystal structures with the 2-phenylquinoline fragment found no entries with the basic structure of (II). *Chemical Abstracts* has confirmed that the compound represents a new, hitherto unknown, ring system.

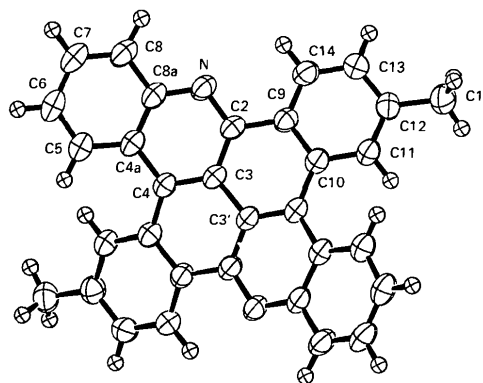


Fig. 1. ORTEP drawing of (IIb). The C and N atoms are shown as 50% ellipsoids; H atoms as 0.1 Å spheres. The C₂ axis is perpendicular to the C3—C3' bond.

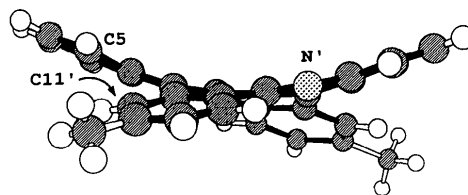


Fig. 2. CHEM3D drawing of (IIb) to illustrate the out-of-plane twist produced by non-bonded interactions. The molecular twofold axis is vertical and in the plane of the paper.

Experimental

Crystal data

C₃₂H₂₀N₂
M_r = 432.52
 Monoclinic
 C2/c
a = 22.566 (5) Å
b = 7.300 (1) Å
c = 13.532 (4) Å
 β = 110.21 (2)°
V = 2085 (2) Å³
Z = 4
D_x = 1.38 Mg m⁻³

Data collection

Enraf-Nonius CAD-4
 diffractometer
 $\theta/2\theta$ scans

Cu *K*α radiation

λ = 1.5418 Å
 Cell parameters from 25
 reflections
 θ = 7.9–25.4°
 μ = 0.58 mm⁻¹
T = 293 K
 Flat hexagonal plates
 0.53 × 0.26 × 0.1 mm
 Light yellow–orange crystals
 from toluene

2130 independent reflections
 1569 observed reflections
 $[I > 3\sigma(I)]$

Absorption correction:
 ψ -scan with data from
 3 reflections
 $T_{\min} = 0.864$, $T_{\max} = 1.0$,
 $T_{\text{av}} = 0.938$
 2370 measured reflections

$R_{\text{int}} = 0.009$ (96 pairs)
 $\theta_{\max} = 69.85^\circ$
 5 standard reflections
 frequency: 60 min
 intensity variation: 0.2–
 3.5, average 1.9%

Refinement

Refinement on F^2
 Final $R = 0.044$
 $wR = 0.061$
 $S = 1.63$

$\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
 Zachariasen

1569 reflections
 195 parameters
 All H-atom parameters re-
 fined
 $\Sigma w(F_o - F_c)^2$ minimized,
 $w = 1/\sigma^2(F)$
 $(\Delta/\sigma)_{\max} = 0.16$

Extinction coefficient:
 $0.327/(6) \times 10^{-6}$
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

C8a—C4a—C4	117.5 (2)	C11—C12—C15	120.6 (2)
C6—C5—C4a	120.6 (2)	C13—C12—C15	121.3 (2)
C5—C6—C7	121.0 (2)	C14—C13—C12	121.0 (2)
C8—C7—C6	120.0 (2)	C13—C14—C9	120.9 (2)
N—C2—C3—C3'	-171.3 (1)	C3—C3'—C2'—C9'	12.4 (2)
N—C2—C3—C4	5.0 (3)	C3—C3'—C4'—C4a'	161.5 (1)
N—C2—C9—C10	169.6 (2)	C3—C3'—C4'—C10	-18.4 (2)
N—C2—C9—C14	-12.9 (3)	C3—C4—C10'—C9'	16.7 (2)
C2—C3—C3'—C2'	180.0 (2)	C3—C4—C10'—C11'	-158.0 (2)
C2—C3—C3'—C4'	3.7 (1)	C4—C3—C3'—C4'	-172.5 (2)
C2—C3—C4—C4a	-14.7 (2)	C4—C10'—C9'—C14'	-178.1 (2)
C2—C3—C4—C10'	165.4 (2)	C4—C10'—C11'—C12'	177.2 (2)
C3—C2—C9—C10	-13.9 (2)	C4a—C4—C10'—C9'	-163.2 (2)
C3—C2—C9—C14	163.5 (2)	C4a—C4—C10'—C11'	22.1 (3)

Data collection: Enraf-Nonius diffractometer software (version 5.0); θ -scan width of $1.5(0.75 + 0.14\tan\theta)^\circ$, scan recorded as 96 steps with two outermost 16-step blocks for background determination, θ -scan speed $8.24\text{--}0.72^\circ \text{ min}^{-1}$; hkl generated to maintain $0 \leq \chi \leq 90^\circ$. All crystallographic calculations were performed with the *TEXSAN* (Molecular Structure Corporation, 1987) system on Digital Equipment Corporation Micro VAX II and VAXStation II computers; structure solution used the *MITHRIL* procedure (Gilmore, 1983) subprogram. Fig. 1 was drawn with the *ORTEP* (Johnson, 1976) subprogram of the *TEXSAN* system; the *PLOTMD* program (Luo, Ammon & Gilliland, 1989) was used to display the drawings on a VAXStation monitor, add labels and prepare files for a Hewlett-Packard Laserjet II printer. Fig. 2 was drawn with the *CHEM3D* program (Cambridge Scientific Computing, 1990) and labeled with the *CHEMDRAW* (Cambridge Scientific Computing, 1989) program on an Apple MacIntosh Ix platform.

The instrumentation used in this work was obtained in part with grants from the National Science Foundation (CHE-84-02155) and the National Institutes of Health (RR-03354).

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71061 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1026]

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

	x	y	z	B_{eq}
N	0.61870 (6)	0.1494 (2)	0.6924 (1)	3.88 (6)
C2	0.55785 (7)	0.1723 (2)	0.6778 (1)	3.44 (6)
C3	0.53382 (6)	0.1722 (2)	0.7621 (1)	3.27 (6)
C4	0.57572 (7)	0.1613 (2)	0.8668 (1)	3.35 (6)
C4a	0.63952 (7)	0.1063 (2)	0.8821 (1)	3.52 (6)
C5	0.68297 (8)	0.0359 (3)	0.9785 (2)	4.09 (7)
C6	0.74215 (8)	-0.0198 (3)	0.9852 (2)	4.64 (8)
C7	0.76138 (8)	-0.0194 (3)	0.8972 (2)	4.83 (8)
C8	0.72067 (8)	0.0525 (3)	0.8032 (2)	4.45 (8)
C8a	0.65826 (7)	0.1065 (2)	0.7919 (1)	3.76 (6)
C9	0.51399 (7)	0.2100 (2)	0.5708 (1)	3.57 (6)
C10	0.44806 (7)	0.2057 (2)	0.5484 (1)	3.46 (6)
C11	0.40806 (8)	0.2592 (2)	0.4467 (1)	3.71 (6)
C12	0.43086 (8)	0.3084 (3)	0.3685 (1)	4.02 (7)
C13	0.49631 (9)	0.3055 (3)	0.3923 (2)	4.53 (8)
C14	0.53696 (8)	0.2576 (3)	0.4911 (2)	4.28 (7)
C15	0.3860 (1)	0.3651 (4)	0.2607 (2)	4.89 (9)

Table 2. Bond lengths (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$) with *e.s.d.*'s in parentheses

The primed atoms are in the twofold-related half of the molecule.			
N—C2	1.327 (2)	C6—C7	1.405 (3)
N—C8a	1.363 (2)	C7—C8	1.360 (3)
C2—C3	1.426 (2)	C8—C8a	1.418 (2)
C2—C9	1.463 (2)	C9—C14	1.395 (3)
C3—C4	1.400 (2)	C9—C10	1.410 (2)
C3—C3'	1.444 (3)	C10—C11	1.408 (2)
C4—C4a	1.437 (2)	C11—C12	1.378 (3)
C4—C10'	1.464 (2)	C12—C13	1.396 (3)
C4a—C5	1.422 (2)	C12—C15	1.510 (3)
C4a—C8a	1.425 (2)	C13—C14	1.373 (3)
C5—C6	1.368 (2)		
C2—N—C8a	117.3 (1)	C7—C8—C8a	120.7 (2)
N—C2—C3	123.2 (2)	N—C8a—C8	116.6 (2)
N—C2—C9	118.3 (2)	N—C8a—C4a	123.8 (1)
C3—C2—C9	118.5 (1)	C8—C8a—C4a	119.5 (2)
C4—C3—C2	119.9 (1)	C14—C9—C10	119.5 (2)
C4—C3—C3'	120.7 (2)	C14—C9—C2	120.4 (2)
C2—C3—C3'	119.3 (2)	C10—C9—C2	120.1 (2)
C3—C4—C4a	116.4 (2)	C11—C10—C9	117.8 (2)
C3—C4—C10'	118.5 (1)	C11—C10—C4	122.8 (1)
C4a—C4—C10'	125.1 (1)	C9—C10—C4	119.2 (2)
C5—C4a—C8a	117.9 (2)	C12—C11—C10	122.6 (2)
C5—C4a—C4	124.3 (2)	C11—C12—C13	118.1 (2)

References

- Cambridge Scientific Computing (1989). *CHEMDRAW. Desktop Publishing for Chemists*. Version 2.1.3. Cambridge Scientific Computing, 875 Massachusetts Avenue, Cambridge, MA, USA.
- Cambridge Scientific Computing (1990). *CHEM3D. Molecular Modeling System*. Version 3.0. Cambridge Scientific Computing, 875 Massachusetts Avenue, Cambridge, MA, USA.
- Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. Univ. of Glasgow, Scotland.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Luo, J., Ammon, H. L. & Gilliland, G. L. (1989). *J. Appl. Cryst.* **22**, 186.
- Molecular Structure Corporation (1987). *TEXSAN. TEXRAY Structure Analysis Package*. Version 2.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Still, C. (1990). *MACROMODEL. Columbia Chemistry Molecular Modelling System*. Version 3.0. Columbia University, New York, NY, USA.