COMMUNICATION

Crystal Study of N,N′-diphenyl-N,N′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine

Jung-An Cheng · Pi-Ju Cheng

Abstract The structure of N,N′-diphenyl-N,N′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (NPB) with two molecules in the asymmetric unit, was solved and refined to a final R factor of 0.0434. The compound crystallized in the triclinic crystal system, space group $P-1$, $Z = 2$, $V = 1597.0(3)$ $Å^3$ with unit cell parameters $a = 10.3077(10)$ Å, $b = 11.3545(11)$ Å, $c = 14.4778(14)$ Å, $\alpha = 82.339(2)°$, $\beta = 77.657(2)°$, and $\gamma = 75.526(2)°$. The two molecules in the asymmetric unit differed in the orientation of their triarylamino groups. The biphenyl group in the central structure is coplanar, and the angle between the least-square planes of the two six-carbon rings of the biphenyl moiety is zero degree. The packing of the molecules in the lattice is mainly due to the naphthyl-to-naphthyl π–π interaction with a distance of 3.861 Å.

Keywords OLED · NPB · Single-crystal · Hole-transporting

Introduction

N,N′-diphenyl-N,N′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (NPB), shown in Fig. 1, is a well-known hole-transporting material in organic light-emitting diodes (OLEDs), since the first high efficiency multi-layered OLEDs based on the small molecules were found [1]. Due to excellent hole mobility [2], high glass transition temperature (T_g), and stable thin-film morphology during thermal deposition

J.-A. Cheng (✉) · P.-J. Cheng
Department of Photonics and Display Institute,
National Chiao Tung University, Hsinchu 30010,
Taiwan, ROC
e-mail: jacheng.ac89g@nctu.edu.tw

[3], NPB has been widely utilized and applied in flat panel displays (FPDs). Despite the importance of the archetype hole transport molecule NPB in OLEDs, relatively few studies of its fundamental molecular properties have appeared in the literature [4–6], and little has been reported concerning the molecular geometry and molecular packing of NPB. In this study, we report the crystal and molecular structure of NPB, which was obtained by thermal deposition in vacuum process. We will also summarize some results on the structures from the viewpoint of the steric influence on molecular conformation.

Experimental Section

NPB is prepared according to reference [7], and the crystal was grown by thermally evaporating NPB in the vacuum chamber at 523 K/36 mtorr.

Crystallography

A suitable colorless crystal with dimensions of 0.10 × 0.10 × 0.10 mm was selected for indexing and intensity data collection on a Siemens SMART CCD diffractometer equipped with a normal-focus, 3-kW sealed-tube X-ray source. Intensity data was collected at 295(2) K in 2359 frames with ω scans (width 0.30° per frame). Multi-scan absorption corrections based on symmetry equivalents were applied ($T_{min, max} = 0.926, 0.986$) [8] to the 19168 reflections collected ($2\theta_{max} = 56.66°$), 7920 unique reflections were observed [$I > 2\sigma - (I)$] after data reduction. The structure was solved by direct methods using SHELXS97 [9] and refined by SHELXL97 [10]: C and N atoms in the framework were found in difference Fourier maps. There are two NPB molecules per unit cell. The final cycles
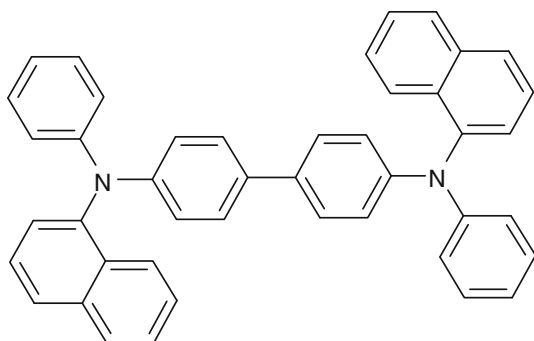
Fig. 1 The chemical structure of NPB

of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The final difference Fourier maps were flat ($\triangle\rho_{max}$, $_{min}$ = 0.13, −0.14 e/Å^3). All calculations were performed using SHELXTL Version 5.1 software package [11]. Figure 2 shows the final ORTEP plot. A summary of crystal data is given in Table 1, fractional coordinates and equivalent isotropic thermal parameters in Table 2.
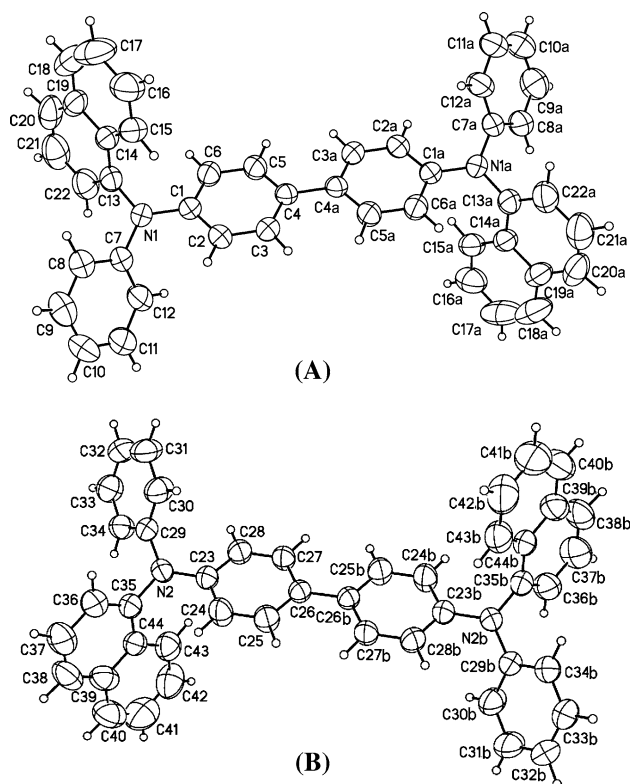

(A)

(B)

Fig. 2 Two independent molecules, A and B, of NPB, showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) −x + 1, −y + 1, −z; (ii) −x, −y + 2, −z + 1.]

Table 1 Crystal data and structure refinement for NPB

Empirical formula	$C_{44}H_{32}N_2$
Formula weight	588.72
Temperature (K)	295 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P - 1$
Unit cell dimensions,	a = 10.3077 (10) Å, α = 82.339 (2)^o
	b = 11.3545 (11) Å, β = 77.657 (2)^o
	c = 14.4778 (14) Å, γ = 75.526 (2)^o
Volume (Å^3)	1597.0 (3)
Z	2
Density (Mg m^{-3})	1.224
Absorption coefficient (mm^{-1})	0.071
$F(000)$	620
Crystal size (mm^3)	0.10 × 0.10 × 0.10
Theta range for data collection	1.44–28.33^o
Index ranges	−13 ≤ h ≤ 13, −15 ≤ k ≤ 15, −19 ≤ l ≤ 19
Reflections collected	19168
Independent reflections	7920 [R(int) = 0.0638]
Completeness to theta = 28.33°	99.5%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7920/0/415
Goodness-of-fit on F^2	0.713
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0434, wR_2 = 0.0709
R indices (all data)	R_1 = 0.1908, wR_2 = 0.0966
Largest diff. peak and hole (eÅ^{-3})	0.145 and −0.124

Results and Discussion

The single-crystal structure of NPB molecules and related information in bond lengths and angles are important for understanding intermolecular interaction, fluorescence, and molecular film characteristics in OLEDs. Selected geometric parameters for NPB are given in Table 3. In the structure, the asymmetric unit consists of two independent molecules, A and B as shown in Fig. 2, and the naphthyl groups are located *trans* to each other with respect to the biphenyl spacer. Besides, the individual aryl rings are essentially planar and resulting in co-planar π–π interactions across the C–C inter-ring bond. The magnitude of this twist is equivalent to the two independent molecules, such that the angle between the least-square planes of the two six-carbon rings of the biphenyl moiety is zero degree, in good agreement with the values obtained in a recent theoretical study [12] and with the neutron single-crystal

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for NPB

	x	y	z	U(eq)		x	y	z	U(eq)
N(1)	3881(2)	1132(2)	1646(1)	59(1)	C(22)	3254(3)	−463(2)	1009(2)	76(1)
N(2)	1262(2)	6302(2)	3206(1)	62(1)	C(23)	904(2)	7336(2)	3722(2)	53(1)
C(1)	4216(2)	2212(2)	1165(2)	50(1)	C(24)	1020(2)	7256(2)	4661(2)	70(1)
C(2)	4817(2)	2908(2)	1590(2)	56(1)	C(25)	682(2)	8292(2)	5141(2)	70(1)
C(3)	5124(2)	3977(2)	1127(2)	54(1)	C(26)	189(2)	9449(2)	4740(2)	47(1)
C(4)	4845(2)	4415(2)	235(2)	46(1)	C(27)	98(2)	9507(2)	3790(2)	59(1)
C(5)	4243(2)	3707(2)	−175(1)	57(1)	C(28)	447(2)	8487(2)	3297(2)	64(1)
C(6)	3929(2)	2635(2)	276(2)	58(1)	C(29)	708(2)	6282(2)	2393(2)	54(1)
C(7)	4585(2)	449(2)	2349(2)	58(1)	C(30)	−674(2)	6725(2)	2406(2)	75(1)
C(8)	3881(2)	−7(2)	3176(2)	71(1)	C(31)	−1184(2)	6773(2)	1596(2)	89(1)
C(9)	4586(3)	−637(2)	3860(2)	98(1)	C(32)	−359(3)	6366(2)	777(2)	81(1)
C(10)	5963(4)	−791(3)	3741(3)	118(1)	C(33)	996(3)	5894(2)	778(2)	79(1)
C(11)	6655(3)	−364(3)	2915(3)	113(1)	C(34)	1528(2)	5850(2)	1575(2)	66(1)
C(12)	5978(2)	233(2)	2215(2)	86(1)	C(35)	2168(2)	5219(2)	3518(2)	60(1)
C(13)	2879(2)	643(2)	1380(2)	59(1)	C(36)	1716(2)	4178(2)	3818(2)	75(1)
C(14)	1509(2)	1287(2)	1522(2)	59(1)	C(37)	2579(3)	3115(2)	4133(2)	92(1)
C(15)	1055(2)	2419(2)	1934(2)	66(1)	C(38)	3876(3)	3105(2)	4154(2)	90(1)
C(16)	−287(3)	2986(2)	2070(2)	89(1)	C(39)	4401(3)	4154(3)	3847(2)	75(1)
C(17)	−1237(3)	2482(4)	1812(2)	116(1)	C(40)	5768(3)	4157(3)	3851(2)	104(1)
C(18)	−830(4)	1424(4)	1416(2)	108(1)	C(41)	6240(3)	5162(4)	3531(3)	125(1)
C(19)	533(3)	760(3)	1268(2)	71(1)	C(42)	5416(3)	6209(3)	3189(2)	104(1)
C(20)	981(4)	−392(3)	885(2)	92(1)	C(43)	4089(3)	6264(2)	3171(2)	80(1)
C(21)	2312(4)	−988(3)	766(2)	95(1)	C(44)	3545(2)	5226(2)	3511(2)	59(1)

Table 3 Selected geometric parameters (Å,°)

N1–C1	1.412(2)	N2–C23	1.405(2)
N1–C7	1.408(2)	N2–C(29	1.419(2)
N1–C13	1.427(2)	N2–C35	1.431(2)
C4–C4a	1.483(3)	C26–C26b	1.472(4)
C1–N1–C7	121.81(18)	C23–N2–C29	121.77(19)
C1–N1–C13	120.48(18)	C23–N2–C35	119.75(18)
C7–N1–C13	117.54(17)	C29–N2–C35	118.43(18)
C1–N1–C7–C8	43.39(18)	C23–N2–C29–C30	44.96(19)
C1–N1–C13–C14	66.66(19)	C23–N2–C35–C36	65.64(19)
C7–N1–C1–C2	26.22(18)	C29–N2–C23–C24	23.48(19)
C7–N1–C13–C14	61.96(18)	C29–N2–C35–C36	63.22(18)
C13–N1–C1–C2	21.31(19)	C35–N2–C23–C24	20.98(19)
C13–N1–C7–C8	48.16(18)	C35–N2–C29–C30	47.43(18)
C3–C4–C4a–C5a	1.10(2)	C25–C26–C26b–C27b	1.48(2)
C5–C4–C4a–C3a	1.10(2)	C27–C26–C26b–C25b	1.48(2)

diffraction data of the unsubstituted biphenyl structure [13].

The independent N atoms of molecules A and B are nominally sp^3 hybridized, but with some planarization of the molecule to take advantage of the resonance delocalization with the aryl rings, which leads to C–N–C bond angles close to 120°, displaying features of sp^2 hybridization. The angle sums around these N atoms are ca 359.83° for the atom N1 and ca 359.95° for the atom N2 (Table 3). Molecular orbital calculations also revealed that the highest occupied molecular orbital (HOMO) is strongly delocalized across all aryl rings of the NPB molecule, with significant contributions from the lone pair electrons of the nitrogen [5, 14]. This geometric feature of NPB molecules in the crystal lattice (similar to that of radical cation state, i.e. sp^2 hybridization and a planar conformation) provides favorable conditions for geometric reorganization during the charge-transfer process [15]. The N–C bond lengths vary from 1.405(2) to 1.431(2) Å, which are in agreement with the experimental crystal structure of triphenylamine [16]. The three aryl rings connected to each N atom adopt a propeller-like orientation. Their corresponding torsion angles (the plane of the rings with respect to the plane defined by the N atom and its three attached C atoms) for N1 and N2 are measured at 21.31–66.66° and 20.98–65.64°, respectively, and summarized in Table 3. The twisted conformation which results from the steric effect of the H atoms in the ortho positions of the phenyl and naphthyl rings can protect the N atoms from chemical attack, e.g. H-atom donors etc., to close the hole-transport function. As a result, NPB has an excellent lifetime when
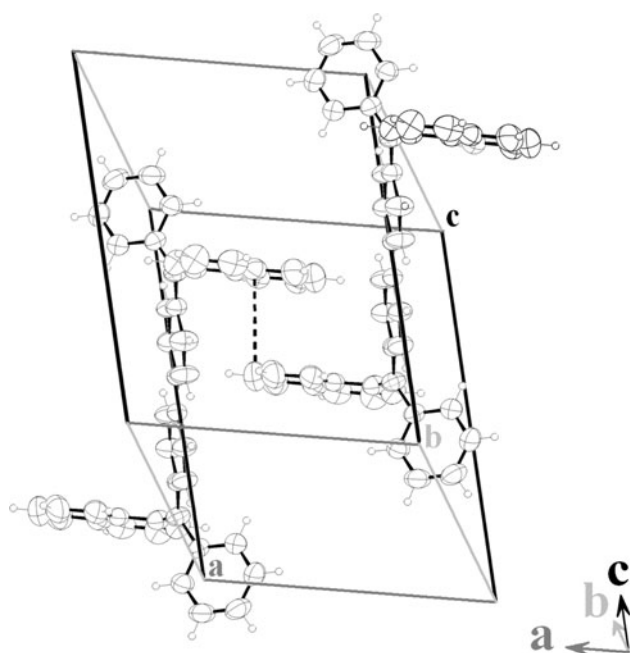
Fig. 3 Part of a stack of molecules of NPB, propagated in the c direction. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms are shown as spheres of arbitrary radii. The dashed line indicates the shortest contact between two naphthyl planes

used as a hole-transporting material during the electroluminescence process.

In the crystal structure of the title compound, a major feature is the naphthyl-to-naphthyl stacking of molecules related to one another by a cell translation, thus forming stacks that propagate in the *c* direction (Fig. 3). Taking account of the angle of the planes relative to the c cell edge, of the order of 72.48°, the repeat distance of 3.861 Å corresponds to an interplanar separation of ∼3.5 Å, which is consistent with the requirements of π–π stacking and clearly accommodates the distance of 3.4 Å required for overlapping π-aromatic ring systems [17].

In addition, molecules carrying triaryl groups, –NAr₃, often engage in multiple phenyl embraces (MPE), where the phenyl rings of two groups (Ar₃N–) are interleaved such that six and/or four edge-to-face aryl–aryl interactions are established [18, 19]. A prevalent MPE is either the sextuple phenyl embrace (SPE) or the quadruple phenyl embrace (QPE). The former has net attractive energies in the range from 60 to 85 kJ mol^{-1} and N···N separations in the range of 6.4–7.4 Å [13, 14, 20], while the latter involves two phenyl groups on each partner [15, 21]. Furthermore, QPEs frequently occur at relatively longer N···N separations and have lower attractive energies. In Fig. 3, the aryl rings of two molecules are interweaved in such a way that total of six edge-to-face aryl–aryl interaction were established. The geometry and the N···N

separation of 6.04–6.63 Å are similar to those of SPE. Each SPE dimer is in contact with two neighboring molecules at N···N separation 8.73 Å and showed a weak QPE interaction.

Supplementary Material

References

1. Tang CW, VanSlyke SA (1987) Appl Phys Lett 51:913
2. Deng Z, Lee ST, Webb DP, Chan YC, Gambling WA (1999) Synth Met 107:107
3. Avendano FM, Forsythe EW, Gao Y, Tang CW (1999) Synth Met 102:910
4. Halls MD, Tripp CP, Schlegel HB (2001) Phys Chem Chem Phys 3:2131
5. Seo JH, Kim CY, Kang SJ, Yoo KH, Whang CN, Moewes A, Chang GS (2007) J Chem Phys 126:064706
6. Wang BC, Liao HR, Chang JC, Chen L, Yeh JT (2007) J Lumin 124:333
7. Yamamoto T, Nishiyama M, Koie Y (1998) Tetrahedron Lett 39:2367
8. Sheldrick GM (1995) SADABS. Siemens analytical X-ray instrument division, Madison, WI
9. Sheldrick GM (1990) SHELXS97, program for the crystal structure solution. University of Göttingen, Germany
10. Sheldrick GM (1997) SHELXL97, program for the crystal structure refinement. University of Göttingen, Germany
11. Sheldrick GM (1998) SHELXTL programs, version 5.1. Bruker AXS, Madison, WI
12. Lin BC, Cheng CP, Lao ZPM (2003) J Phys Chem A 107:5241
13. Cailleau H, Baudour JL (1979) Acta Crystallogr B35:426
14. Sugiyama K, Yoshimura D, Miyamae T, Miyazaki T, Ishii H, Ou-Chi Y, Seki K (1998) J Appl Phys 83:4928
15. Malagoli M, Brédas JL (2000) Chem Phys Lett 327:13
16. Sobolev AN, Belsky VK, Romm IP, Chernikova YN, Guryanova EN (1985) Acta Crystallogr C41:967
17. Pauling L (1967) The nature of chemical bond. Cornell University Press, Ithaca, NY
18. Dance I, Scudder M (1996) Chem Eur J 2:481
19. Dance I, Scudder M (1996) J Chem Soc Dalton Trans 3755
20. Scudder M, Dance I (1998) J Chem Soc Dalton Trans 3167
21. Gareth RL, Dance I (2000) Inorg Chim Acta 306:160