

Non-merohedrally twinned crystals of *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine: an excellent triphenylamine-based hole transporter

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N,N'-Bis(3-methylphenyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (TPD), C₃₈H₃₂N₂, crystallizes in the monoclinic space group *P*₂₁ with a pseudo-orthogonal lattice, rather than the previously reported orthorhombic space group *P*₂₁2₁2₁ [Kennedy, Smith, Tackley, David, Shankland, Brown & Teat (2002). *J. Mater. Chem.* **12**, 168–172]. The asymmetric unit consists of two independent molecules, *A* and *B*, which are arranged along the [100] direction to form vertical layers of alternately stacked *A* and *B* molecules. Molecule *A* shows a great deal of rotational movement in the four terminal aryl rings, resulting in two disordered tolyl groups split over two sites, while molecule *B* exhibits an almost *cis* configuration of the two terminal tolyl groups with respect to these ring planes.

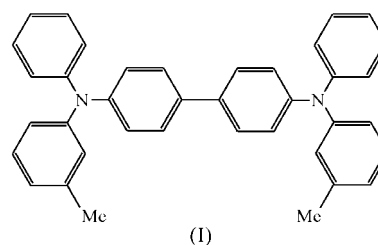
Comment

The crystal structure of the title compound (TPD), (I), was first reported from a synchrotron single-crystal diffraction experiment with a microcrystal, on Station 9.8 of the Daresbury SRS, based on an orthorhombic structure of (I) (Kennedy *et al.*, 2002). The data were deposited in the Cambridge Structural Database (Allen, 2002; reference No. 174 279), although the coordinates of several atoms were incorrect. The aim of the present work was to provide a complete structural analysis to correct this error in the existing literature and to support the findings obtained from density-functional theory for predicting the reorganization energy (Malagoli & Brédas, 2000; Lin *et al.*, 2003).

Colorless crystals of (I), obtained in this study with more careful recrystallization experiments from morpholine, revealed that the compound crystallizes in the monoclinic space group *P*₂₁ with a pseudo-orthogonal lattice at 90 (2) K, rather than the orthorhombic space group *P*₂₁2₁2₁ (Kennedy *et al.*, 2002). The β angle of monoclinic *P*₂₁ is close to 90° and

thus the crystals appear orthorhombic when twinned. The twinning phenomenon of (I) was frequently observed during our X-ray investigations. It is not possible to prevent twinning, even under idealized conditions such as low temperature, slow crystal growth or crystallization from different solvents. It is quite clear that the second polymorph of (I) proposed by Kennedy *et al.* (2002) does not exist, because the simulated profile of the monoclinic *P*₂₁ structure has completely accounted for the peaks in the powder diffraction data. The additional peaks mentioned by Kennedy *et al.* (2002) arise from the reduction of symmetry from orthorhombic to monoclinic, with $\beta = 90.602^\circ$, rather than from a form II of (I).

Selected geometric parameters for (I) are given in Table 1. In the structure of (I), the asymmetric unit consists of two independent molecules, *A* and *B* (Fig. 1), which are arranged along [100] to form vertical layers of alternately stacked *A* and *B* molecules (Fig. 2). Molecule *A* shows a great deal of rotational movement in the four terminal aryl rings, resulting in two disordered tolyl groups split over two sites, the occupancies of which refined to 64.4 (8)% for atom C32*B* and 35.6 (8)% for atom C32*A*. Molecule *B* exhibits a nearly *cis* configuration of the two terminal tolyl groups with respect to these ring planes.



Although the individual rings are essentially planar, the two central biphenyl groups are twisted as a consequence of the H atoms in the *ortho* positions, which introduce repulsive steric forces, resulting in non-planar π - π interactions across the C—C inter-ring bond. The magnitude of this twist is almost equivalent for the two independent molecules, such that the torsion angles are C16—C17—C20—C21 = 36.5 (5)°, C18—C17—C20—C25 = 36.2 (5)°, C56—C55—C58—C63 = 36.4 (5)° and C54—C55—C58—C59 = 35.7 (5)°. The inter-ring distances are C17—C20 = 1.487 (4) Å and C55—C58 = 1.485 (4) Å, in close agreement with the values obtained in a recent theoretical study (Lin *et al.*, 2003) and with the neutron single-crystal diffraction data of an unsubstituted biphenyl (Cailleau & Baudour, 1979).

The four 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 benzene 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° for atoms N1 and N4, and *ca* 360° for atoms N2 and N3 (Table 1). Molecular-orbital calculations also revealed that the highest occupied molecular orbital (HOMO) of (I) is strongly delocalized across all benzene rings of the molecule of (I), with significant contributions from the lone-pair electrons of the nitrogen

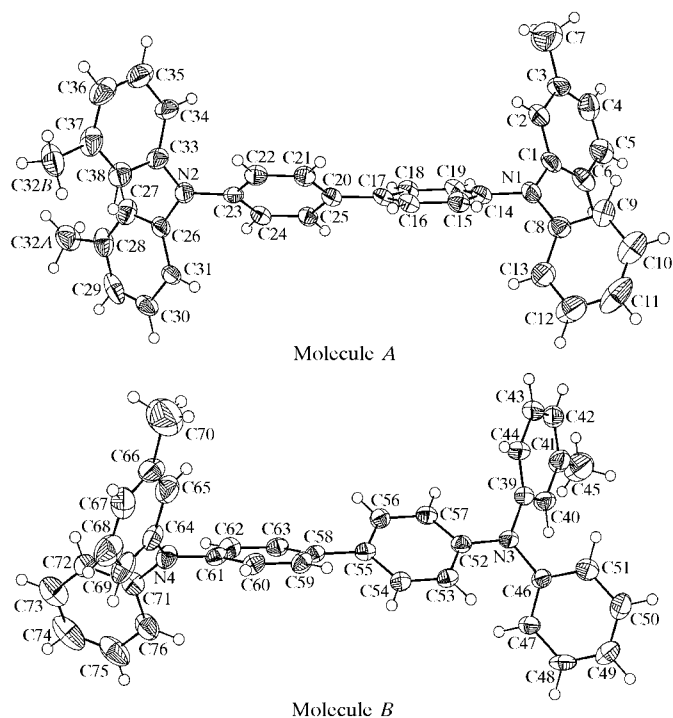


Figure 1
The two independent molecules, *A* and *B*, of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary size. Atom C32*B* is modeled at 64.4 (8)% occupancy and atom C32*A* at 35.6 (8)% occupancy. The H atoms bonded to atoms C28 and C37 have been omitted for clarity.

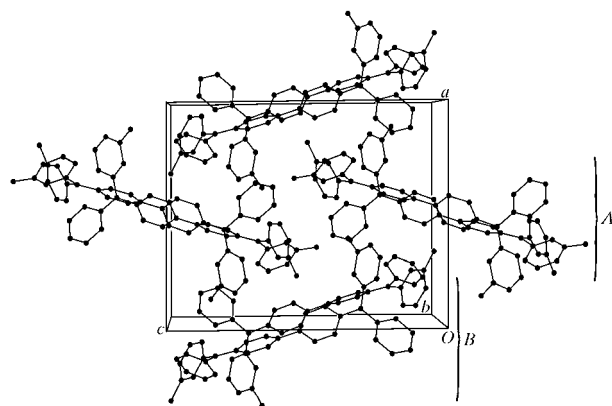


Figure 2
A packing diagram for (I), viewed along *a*, with molecules *A* and *B* alternately stacked parallel to the (100) plane. H atoms have been omitted for clarity.

(Sugiyama *et al.*, 1998). This geometric feature of molecules of (I) in the crystal lattice (similar to that of its radical cation state, *i.e.* sp^2 hybridization and a planar conformation) provides favorable conditions for geometric reorganization during the charge-transfer process (Malagoli & Brédas, 2000). The N—C bond distances vary from 1.415 to 1.430 Å, and these results are in excellent agreement with the experimental crystal structure of triphenylamine (Sobolev *et al.*, 1985).

The three rings connected to each N atom adopt a propeller-like orientation, with torsion angles (the plane of the rings with respect to the plane defined by the N atom and its three attached C atoms) in the range 31.4 (6)–54.0 (5)° for atom N1, 19.0 (5)–57.1 (5)° for N2, 19.4 (5)–55.9 (5)° for N3 and 32.6 (6)–52.9 (4)° for N4. The twisted conformation results from the steric effect of the H atoms in the *ortho* positions of the benzene rings. This twisted conformation can protect the N atoms from chemical attack, *e.g.* H-atom donors *etc.*, to lose the hole-transport function, so that (I) has an excellent lifetime when used as a photoreceptor during the repetitive xerographic cycling process.

Experimental

Colorless crystals of (I) suitable for X-ray diffraction determination were obtained by recrystallization from morpholine through careful evaporation of the solvent. The compound was also recrystallized from other organic solvents. However, smaller twinned crystals were obtained by recrystallization from acetic acid. Powder diffraction patterns indicate that the recrystallized samples contained only one phase of (I).

Crystal data

$C_{38}H_{32}N_2$	$D_x = 1.211 \text{ Mg m}^{-3}$
$M_r = 516.66$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 10 068 reflections
$a = 14.447 (2) \text{ \AA}$	$\theta = 1.4\text{--}29.0^\circ$
$b = 11.0153 (16) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$c = 17.803 (3) \text{ \AA}$	$T = 90 (2) \text{ K}$
$\beta = 90.602 (3)^\circ$	Parallelepiped, colorless
$V = 2833.0 (7) \text{ \AA}^3$	$0.30 \times 0.20 \times 0.20 \text{ mm}$
$Z = 4$	

Table 1

Selected geometric parameters (Å, °).

N1—C8	1.419 (4)	N3—C52	1.415 (4)
N1—C1	1.422 (4)	N3—C46	1.428 (4)
N1—C14	1.429 (4)	N3—C39	1.430 (4)
N2—C33	1.420 (5)	N4—C64	1.416 (4)
N2—C26	1.424 (4)	N4—C61	1.417 (4)
N2—C23	1.428 (4)	N4—C71	1.418 (4)
C17—C20	1.487 (4)	C55—C58	1.485 (4)
C8—N1—C1	120.4 (3)	C52—N3—C46	122.0 (3)
C8—N1—C14	120.3 (3)	C52—N3—C39	120.1 (3)
C1—N1—C14	118.2 (3)	C46—N3—C39	117.7 (3)
C33—N2—C26	118.7 (3)	C64—N4—C61	118.6 (3)
C33—N2—C23	119.8 (3)	C64—N4—C71	120.6 (3)
C26—N2—C23	121.1 (3)	C61—N4—C71	119.9 (3)
C14—N1—C1—C2	54.0 (5)	C52—N3—C39—C44	55.9 (5)
C8—N1—C1—C6	40.5 (5)	C46—N3—C39—C40	50.5 (5)
C14—N1—C8—C13	31.4 (6)	C52—N3—C46—C47	44.0 (5)
C1—N1—C8—C9	45.5 (5)	C39—N3—C46—C51	47.6 (5)
C1—N1—C14—C19	31.7 (5)	C39—N3—C52—C57	19.4 (5)
C8—N1—C14—C15	44.8 (5)	C46—N3—C52—C53	26.0 (5)
C16—C17—C20—C21	36.5 (5)	C54—C55—C58—C59	35.7 (5)
C18—C17—C20—C25	36.2 (5)	C56—C55—C58—C63	36.4 (5)
C33—N2—C23—C22	19.0 (5)	C64—N4—C61—C60	34.4 (5)
C26—N2—C23—C24	27.3 (5)	C71—N4—C61—C62	45.2 (5)
C33—N2—C26—C27	47.7 (5)	C61—N4—C64—C65	52.9 (5)
C23—N2—C26—C31	43.2 (5)	C71—N4—C64—C69	42.3 (5)
C26—N2—C33—C38	49.6 (5)	C64—N4—C71—C72	43.5 (5)
C23—N2—C33—C34	57.1 (5)	C61—N4—C71—C76	32.6 (6)

Data collection

Bruker P4 diffractometer with a SMART APEX CCD detector	10 070 measured reflections
φ and ω scans	10 070 independent reflections
Absorption correction: multi-scan (TWINABS in SAINT-Plus; Sheldrick, 1999)	4919 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.971$, $T_{\max} = 0.995$	$\theta_{\max} = 29.0^\circ$
	$h = -19 \rightarrow 19$
	$k = 0 \rightarrow 15$
	$l = 0 \rightarrow 24$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.063$	$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2]$
$wR(F^2) = 0.130$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.90$	$(\Delta/\sigma)_{\max} < 0.001$
10 070 reflections	$\Delta\rho_{\max} = 0.52 \text{ e } \text{\AA}^{-3}$
735 parameters	$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$

The analyzed crystal was mounted in a sealed glass capillary. We analyzed at least two samples but were unable to find pure untwinned crystals. Many reflections showed a typical split. A twin analysis of all reflections with the TWINABS program (Sheldrick, 1999) revealed twinning with two crystal components for our sample, *i.e.* 28 932 reflections for component 1, 28 809 for component 2 and 3295 for both. Since numerous reflections of this non-merohedral twin resulted in relatively poor data quality due to partial overlapping, an HKLF-5 file was generated for structural refinement, including 12 812 corrected reflections (10 496 reflections from the main component and 2316 overlapping reflections from the twin component); 2742 of these were rejected as systematic absence violations. The ratio of minimum to maximum apparent transmission is 0.8562. A subset of the data from crystals of (I) displayed a twofold axial symmetry with an extinction $0k0$, $k = 2n$, which is characteristic of space groups $P2_1$ (No. 4) or $P2_1/m$ (No. 11). The non-centrosymmetric space group was found to be correct during the structural analysis. However, the refinement was unsatisfactory unless all 10 070 measured reflections which suffered from the non-merohedral twinning effect, treated by the HKLF-5 approach mentioned above, were taken into account. The ratio of the two twin components refined to 0.035 (2) using the BASF instruction. The introduction of twinning reduced the R value from 14.22 to 6.29%. The disordered atoms (C32A and C32B) were

split over two sites, the occupancies of which were refined with anisotropic models to a final occupancy of 0.644 (8) for atom C32B and 0.356 (8) for atom C32A. H atoms were placed in geometrically calculated positions, with aryl C–H distances of 0.95 Å and methyl C–H distances of 0.98 Å, and were isotropically refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aryl C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: enCIFer (Allen *et al.*, 2004) and local programs.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1182). Services for accessing these data are described at the back of the journal.

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