

(4-Chlorophenyl)diphenylamine

Zhi-Qiang Guo,^a Shuo Jin^a and
Bo Liu^{b*}^aCollege of Chemistry and Chemical
Engineering, Shanxi University, Taiyuan
030006, People's Republic of China, and ^bThe
Institute of Modern Chemistry, Shanxi
University, Taiyuan 030006, People's Republic
of ChinaCorrespondence e-mail:
guozhiqiang7988@yahoo.com.cn

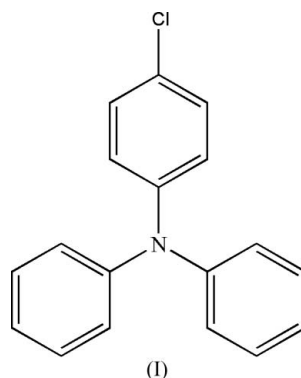
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.056
 wR factor = 0.125
Data-to-parameter ratio = 14.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_{18}\text{H}_{14}\text{ClN}$, is an intermediate in the preparation of a hole-transporting material. The molecule is constructed from three benzene ring systems through C—N bonds.

Comment

High-purity triarylamines have been employed in xerographic photoreceptors where, as concentrated solid solutions in polymeric transport layers, they function as efficient hole conductors (Law, 1993). The latent electrostatic images created by injected positive charge migrates through such layers under the influence of an applied electric field (Abkowitz *et al.*, 1991). Since triarylamines possess an easily accessible oxidation potential and on hole injection give up a non-bonding electron, generating amine cation radicals, this process occurs readily. Triarylamines are also important in a number of emerging technologies (Tanaka *et al.*, 1996). They are also used as non-linear optical chromophores in the design of integrated electro-optic switches and modulators (Miller *et al.*, 1995). Many luminescent materials can be prepared from the title compound, (I), due to its versatility and utility in organic synthesis. Here we report the crystal structure of (I).



The molecule of (I) has three benzene rings which are connected to a central N atom (Fig. 1). The C1—N1 bond length is shorter than the C7—N1 and C13—N1 bond lengths (Table 1). The difference is considered to be the result of the Cl atom attached to the C1—C6 benzene ring. Atoms N1, C1, C7 and C13 are coplanar, with a mean deviation from the plane of 0.0031 Å. The plane of the four atoms form dihedral angles of 31.8, 38.8 and 47.2° with the C1-, C7- and C13-phenyl rings, respectively. The C—N—C angles (Table 1) are in agreement with the published results of theoretical calculations (Sancho-García *et al.*, 2004) and experiments (Hayes *et al.*, 1980).

Received 19 May 2006

Accepted 21 June 2006

Experimental

To a 500 ml round-bottomed flask containing 70 ml of toluene equipped with a mechanical stirrer, a nitrogen gas purge, and a Dean-Stark trap under a reflux condenser were added in the following order while maintaining vigorous stirring: 110 mmol of diphenylamine, 110 mmol of 1-chloro-4-iodobenzene, 4 mmol of 1,10-phenanthroline, 4 mmol of cuprous chloride and 860 mmol of potassium hydroxide flakes (Goodbrand & Hu, 1999). The reaction mixture was heated rapidly over the course of 30 min to the reflux temperature of 398 K and maintained at that temperature until qualitative high-performance liquid chromatographic analysis revealed complete conversion; usually 4–5 h are sufficient. The reaction mixture was cooled to 348 K and partitioned between 200 ml of toluene and 150 ml of deionized water. After washing with an additional amount of water, the organic phase was treated with 36 g of Filtrol-24, an acid-leached bentonite clay, and 24 g of Alcoa CG-20 alumina for over 3 h at 348 K. The adsorbents were then removed by hot filtration and the solvent was removed by rotary evaporation. The product was subjected to further purification by hot column chromatography with heptane elution.

Crystal data

$C_{18}H_{14}ClN$	$Z = 4$
$M_r = 279.75$	$D_x = 1.276 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.961(2) \text{ \AA}$	$\mu = 0.25 \text{ mm}^{-1}$
$b = 17.926(3) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 10.204(2) \text{ \AA}$	Block, colorless
$\beta = 90.682(3)^\circ$	$0.50 \times 0.30 \times 0.20 \text{ mm}$
$V = 1456.2(5) \text{ \AA}^3$	

Data collection

Bruker SMART CCD diffractometer	5974 measured reflections
ω scans	2568 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2015 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.755$, $T_{\max} = 0.952$	$R_{\text{int}} = 0.022$
	$\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 0.5699P]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.125$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
2568 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
181 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cl1—C4	1.743 (2)	N1—C7	1.423 (3)
N1—C1	1.407 (3)	N1—C13	1.424 (3)
C1—N1—C7	121.54 (18)	C7—N1—C13	117.95 (18)
C1—N1—C13	120.50 (18)	C3—C4—Cl1	119.7 (2)

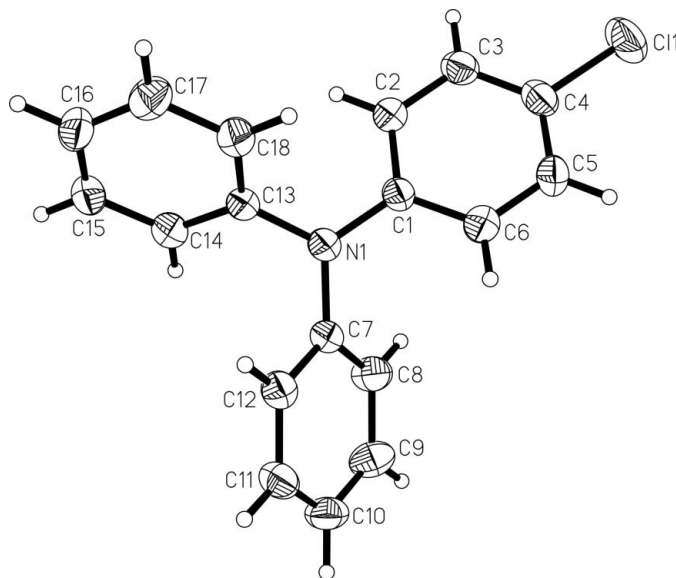


Figure 1

The molecular structure of (I), showing the atom-labeling scheme and 30% probability displacement ellipsoids.

H atoms were placed in idealized positions and allowed to ride on their parent atoms, with C—H = 0.93 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent})$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 1999); software used to prepare material for publication: SHELXTL.

This work was undertaken under the sponsorship of the Natural Science Foundation of China (No. 20372044).

References

- Abkowitz, M., Bassler, H. & Stolka, M. (1991). *Philos. Mag. B*, **63**, 201–220.
- Bruker (2000). SMART (Version 5.0) and SAINT (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
- Goodbrand, H. B. & Hu, N.-X. (1999). *J. Org. Chem.* **64**, 670–674.
- Hayes, K. S., Nagumo, M., Blount, J. F. & Mislow, K. (1980). *J. Am. Chem. Soc.* **102**, 2773–2776.
- Law, K. Y. (1993). *Chem. Rev.* **93**, 449–486.
- Miller, R. D., Lee, V. Y. & Twieg, R. J. (1995). *J. Chem. Soc. Chem. Commun.* pp. 245–246.
- Sancho-García, J. C., Foden, C. L., Grizzi, I., Greczynski, G., de Jong, M. P., Salaneck, W. R., Brédas, J. L. & Cornil, J. (2004). *J. Phys. Chem. B*, **108**, 5594–5599.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). SHELXL97 and SHELXS97. University of Göttingen, Germany.
- Sheldrick, G. M. (1999). SHELXTL. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Tanaka, H., Tokito, S., Taga, Y. & Okada, A. (1996). *J. Chem. Soc. Chem. Commun.* pp. 2175–2176.