

program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXL93*; software used to prepare material for publication: *SHELXL93*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1199). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-(*p*-Tolylamino)benzo-1,3-dioxole

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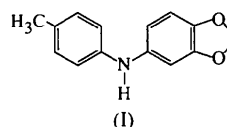
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Abstract

The title compound, C₁₄H₁₃NO₂, is used in the preparation of phenothiazine drugs. The observed structure, with torsion angles of 13.3 (3) and 37.4 (3)° about the C_{aryl}—N bonds, has been used for semi-empirical calculations. The resulting predictions are in accord with the observed selectivity of the reaction.

Comment

Phenothiazine derivatives are well known therapeutic agents (Gupta, 1988) and we have recently described the preparation of some pyrazolo[3,4-*b*]- and [4,3-*c*]phenothiazines (Boyer, Galy & Barbe, 1995). The sulfur thionation of the intermediate diarylamine can lead to two isomers depending on the cyclization position [C2 or C5 according to Fig. 1 labelling; these are the two *ortho* positions on the second ring (*B*)], resulting in a linear or stepped arrangement of the rings in the final product. The torsion angles C9—C8—N—C1 and C2—C1—N—C8 for the title compound, (I), are 13.3 (3) and 37.4 (3)°, respectively.



From the Cambridge Structural Database (Allen & Kennard, 1993), we extracted some diarylamines in order to compare these torsion angles with those for similar compounds. Table 2 shows diphenylamines substituted exclusively in the *para* position on ring *A* and either the *meta* or *para* position on ring *B*. The torsion angles and the distances between *ortho* atoms are also given in Table 2. Comparison of these ten derivatives shows no structural correlation between the type of substituents and the orientation of the reaction.

In light of these results, we were interested in the potential charge delocalization of the benzodioxole moiety, especially for the C2 and C5 atoms. We used *AM1* semi-empirical calculations (Dewar, Zoebisch, Healy & Stewart, 1985) with our crystallographically determined molecular geometry and obtained charges of

−0.144 and −0.192 e for C2 and C5, respectively, with a total energy of 132.96 kcal mol^{−1} (1 cal = 4.184 J). Next, we changed the C8—N—C1—C2 torsion angle by 180° in order to calculate the corresponding delocalized charges for the linear *N*-arylamine and obtained values of −0.153 (C2) and −0.176 e (C5), with a calculated energy of 131.20 kcal mol^{−1}. From these results, the predicted position of cyclization in the thionation is C5, to give a linear tetracycle; this prediction was verified experimentally with the observed formation of only one isomer, the linear one.

The crystallographic study of 5-(*p*-tolylamino)benzo-1,3-dioxole has thus provided us with information about the last step of the synthetic pathway for phenothiazines.

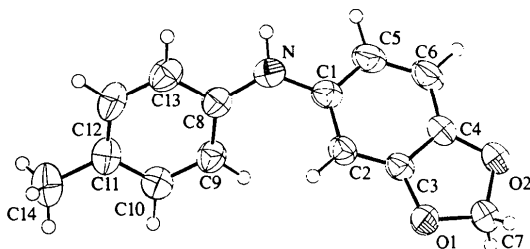


Fig. 1. A perspective view of (I) showing the atom-labelling scheme and displacement ellipsoids at 50% probability for non-H atoms.

Experimental

Crystals of (I) were obtained by slow evaporation of a methylene chloride solution.

Crystal data

C₁₄H₁₃NO₂
M_r = 227.27
 Monoclinic
*C*2/*c*
a = 19.1860 (6) Å
b = 6.4523 (4) Å
c = 20.9867 (6) Å
 β = 118.69 (2)°
V = 2279 (3) Å³
Z = 8
D_x = 1.32 Mg m^{−3}
D_m = 1.35 Mg m^{−3}
D_m measured by flotation in
 C₂H₄Cl₂ and C₂H₃Cl₃

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 2034 measured reflections
 1793 independent reflections
 1299 reflections with
I > 3 σ (*I*)

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 25
 reflections
 θ = 10–18°
 μ = 0.083 mm^{−1}
T = 294 K
 Prism
 0.80 × 0.60 × 0.40 mm
 Yellow

*R*_{int} = 0.019
 θ_{\max} = 23.98°
h = −21 → 19
k = 0 → 7
l = 0 → 23
 3 standard reflections
 frequency: 60 min
 intensity decay: 1.2%

Refinement

Refinement on *F*²
R = 0.038
wR = 0.048
S = 1.725
 1299 reflections
 193 parameters
 H atoms refined with fixed
*U*_{iso}

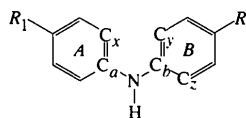
$w = 4F_o^2 / [\sigma^2(F_o^2) + 0.0016F_o^4]$
 $(\Delta/\sigma)_{\max} = 0.323$
 $\Delta\rho_{\max} = 0.07 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.09 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected torsion angles (°)

C8—N—C1—C2	37.4 (3)	C1—N—C8—C9	13.3 (3)
C8—N—C1—C5	−146.8 (2)	C1—N—C8—C13	−168.7 (2)

Table 2. Comparison of the conformation between the two aromatic rings for substituted diphenylamines

p and *m* correspond to the *para* or *meta* position of substituent *R*₂ on ring *B*. Torsion angles τ_a and τ_b are C_x—C_a—N—C_b and C_a—N—C_b—C_y, respectively.



<i>R</i> ₁	<i>R</i> ₂	C _x ···C _y (Å)	C _x ···C _z (Å)	τ_a (°)	τ_b (°)	Reference
H	H	3.04	4.42	−41.5	−8.6	(a)
NO	H	3.17	4.07	9.3	52.7	(b)
NO ₂	<i>p</i> -NCS	3.08	4.37	16.5	36.7	(c)
Phthalimide	H	3.13	4.29	5.6	−43.3	(d)
Cl	<i>p</i> -Cl	3.32	4.30	−23.0	−39.1	(e)
H	<i>p</i> -NHPh	3.16	4.48	−27.0	−8.9	(f)
H	<i>m</i> -NHPh	3.22	4.38	−38.1	−20.4	(g)
(CN) ₂ C=CCN	H	3.14	4.28	−1.3	39.5	(h)
'Bu	H	3.22	4.44	57.4	4.4	(i)
NMe ₂	<i>p</i> -NMe ₂	3.04	4.28	25.1	25.2	(j)

References: (a) Brassy & Mornon (1972); (b) Dhaneshwar, Naik & Tavale (1991); (c) Hardgrove, Einstein & Wei (1983); (d) Magomedova, Ginzburg, Novakovskaya & Zvonkova (1978); (e) Plieth & Ruban (1961); (f) Povet'eva, Chetkina & Kopylov (1976); (g) Povet'eva, Chetkina & Kopylov (1977); (h) Popov, Chetkina & Kotov (1978); (i) Starikova, Obodovskaya, Ivanov & Pokrovskaya (1989); (j) Toman, Ocenaskova & Huml (1967).

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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