

**Experimental**

Colourless rods of (1) (m.p. 397–402 K) were grown from petrol.

*Crystal data*

C<sub>20</sub>H<sub>23</sub>ClO<sub>6</sub>Si

*M<sub>r</sub>* = 422.94

Monoclinic

*P*2<sub>1</sub>

*a* = 8.137 (2) Å

*b* = 12.363 (2) Å

*c* = 10.537 (2) Å

$\beta$  = 98.77 (2)°

*V* = 1047.6 (4) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.341 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Cu *K*α (Ni-filtered) radiation

$\lambda$  = 1.5418 Å

Cell parameters from 25 reflections

$\theta$  = 25–30°

$\mu$  = 2.453 mm<sup>-1</sup>

*T* = 293 (2) K

Rod

0.40 × 0.20 × 0.15 mm

Colourless

*Data collection*

Enraf–Nonius CAD-4S diffractometer

$\omega/2\theta$  scans

Absorption correction:

Gaussian (SHELX76);

Sheldrick, 1976)

*T<sub>min</sub>* = 0.50, *T<sub>max</sub>* = 0.72

1957 measured reflections

1832 independent reflections

1726 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.0511

$\theta_{\max}$  = 63.96°

*h* = 0 → 9

*k* = 0 → 14

*l* = -12 → 12

3 standard reflections

frequency: 160 min

intensity decay: <2%

*Refinement*

Refinement on *F*<sup>2</sup>

*R*(*F*) = 0.0397

*wR*(*F*<sup>2</sup>) = 0.1046

*S* = 1.235

1832 reflections

346 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.4093P]$

where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> = 1.010

$\Delta\rho_{\max} = 0.238 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.354 \text{ e } \text{Å}^{-3}$

Extinction correction:

SHELXL93

Extinction coefficient:

0.0073 (10)

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Absolute configuration:

Flack (1983)

Flack parameter = 0.01 (3)

The title structure was solved by direct methods using SHELXS86 (Sheldrick, 1990). Refinement was performed with SHELXL93 (Sheldrick, 1993) using anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for the H atoms. All calculations were carried out on a VAXstation 4000VLC computer system.

Data collection: CAD-4/VAX (Enraf–Nonius, 1989). Cell refinement: CAD-4/VAX. Molecular graphics: ZORTEP (Zsolnai, 1994). Software used to prepare material for publication: SHELXL93.

The authors acknowledge support from the Australian Research Grants Scheme and the Australian Postgraduate Award (to AGR).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: OA1012). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1997). **C53**, 387–391

**(1*R*,1*R'*)-2-*exo*-Mercapto-2'-thioxo-3-*exo*,3'-*exo*-bibornane, 2-Dehydro-2,2'-*exo*-epidithio-3,3'-bibornane and 2-*endo*,2'-*exo*-Epidithio-3,3'-bibornanylidene. Potential Antiviral Agents**

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(Received 8 May 1996; accepted 30 September 1996)

**Abstract**

The compounds 2,2'-*exo*-epidithio-1,1',7,7',7'-hexamethyl-3,3'-bibicyclo[2.2.1]hept-2-ene, C<sub>20</sub>H<sub>30</sub>S<sub>2</sub>, (2), and 2-*endo*,2'-*exo*-epidithio-1,1',7,7',7'-hexamethyl-3,3'-bibicyclo[2.2.1]heptanylidene, C<sub>20</sub>H<sub>30</sub>S<sub>2</sub>, (3), were prepared as potential antiviral agents and their structures were determined by X-ray diffraction. It has been shown previously that there is a relationship between the strain energy of a C—S—S—C group, as measured by its planarity and S—S bond length, and the antiviral activity of the compound containing this group. In

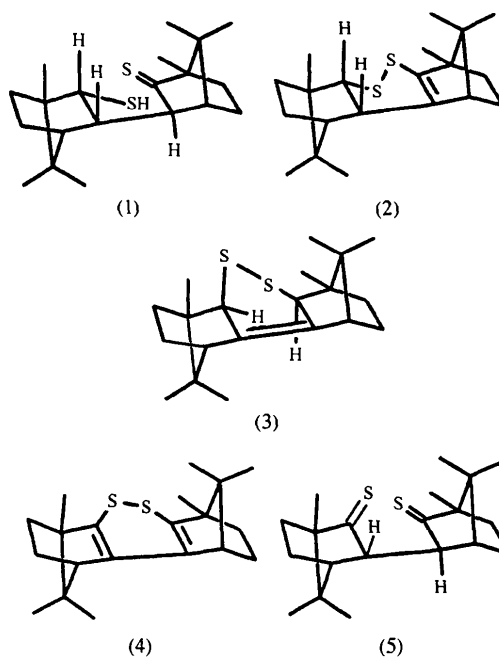
general, the activity increases with the planarity of the group and as the disulfide bond distorts from a 'normal' length. The values of the C—S—S—C torsion angle and S—S bond length for compounds (2) and (3) are 56.1 (1)° and 2.056 (1) Å, and 44.9 (2)° and 2.019 (2) Å, respectively. (1*R*,1'*R'*)-2'-*exo*-Mercapto-1,1',7,7',7'-hexamethyl-3-*exo*,3'-*exo*-bicyclo[2.2.1]heptane-2-thione, C<sub>20</sub>H<sub>32</sub>S<sub>2</sub>, (1), is the intermediate compound necessary to obtain compound (2). The absolute configuration of each of the title compounds was determined from the X-ray studies.

### Comment

This investigation forms part of a study on possible new antiviral agents. It is known that compounds containing a C—S—S—C group have antiviral properties (Block, Guo, Thiruvazhi & Toscano, 1994). It has been shown (Steliou, 1991; Steliou, Gareau, Milot & Salama, 1989) that there is a relationship between the strain energy of the C—S—S—C group, as measured by its planarity and S—S bond length, and the antiviral activity of the compound containing this group. This activity increases with the planarity of the group and as the disulfide bond distorts from a 'normal' length. Our aim was thus to obtain compounds in which the C—S—S—C torsion angle could be modulated by the introduction of some geometrical restrictions.

To define the 'normal' disulfide bond length, the April 1995 version of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) was searched for X—S—S—X acyclic fragments. The torsion angle defined by the fragment was allowed to range between 80 and 100° which minimizes the sulfur-sulfur lone-pair energy interactions. As a result, we obtained a Gaussian distribution of 95 S—S bond lengths with a median value of 2.035 Å and 80% of the observed values found between 2.004 and 2.068 Å.

In order to systematically correlate the biological activities of cyclic 1,2-disulfides with their C—S—S—C strain energies, we prepared compounds (2) and (3), thus completing a series of analogous dithiines including the previously synthesized compound, 2,2'-didehydro-2,2'-*exo*-epidithio-3,3'-bibornane, (4) (Salama, Poirier & Caissie, 1995). These compounds were chosen to carry out this comparative study because their common precursor bithiocamphor, (5) (Campbell & Evgenios, 1973), an enolizable 1,4-dithioketone, exhibits a remarkable synthetic potential because of its ketone-like deprotonation ability. Recently, the synthesis of compound (4) was reported together with its structure determined by X-ray analysis (Schroth, Hintzsche, Spitzner, Irgartinger & Siemund, 1994). The C—S—S—C torsion angle was reported to be 47°, while the S—S bond length was 2.065 Å. Details of the preparation of the title compounds will be published elsewhere (Salama & Poirier, 1997).



Compound (1) (Fig. 1) is the intermediate compound used to obtain compound (2) and was prepared *via* the mono-reduction of (5). The absolute configuration of (1) is 1*R*,2*S*,3*R*,6*R*,12*S*,13*R*,16*R*. The SH group is in an *exo* position in relation to the norbornane skeleton. The norbornane skeletons in all the investigated compounds are no different from those investigated so far (Schroth, Hintzsche, Spitzner, Ströhl & Sieler, 1995; Schroth, Hintzsche, Spitzner, Ströhl, Schmeif & Sieler, 1995; Schroth *et al.*, 1994; Kempe, Sieler, Hintzsche & Schroth, 1993*a,b,c*; Pradhan, Thakker & McPhail, 1987; Catellani, Chiusoli & Sgarabotto, 1982).

All three title compounds crystallized in the space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> [(1) from hexane, and (2) and (3) from ethanol-water (9:1)]. The cell constants do not

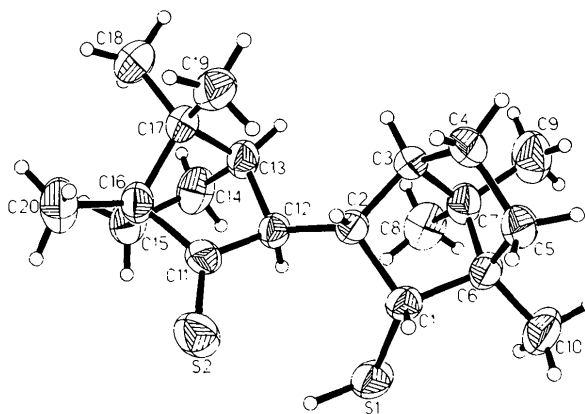


Fig. 1. The molecular structure of compound (1). Displacement ellipsoids are drawn at the 50% probability level.

differ significantly, which suggests that the packing arrangement in each crystal should be similar for these compounds. The packing arrangement for compound (1) is shown in Fig. 2. The projected chain of the molecules is linear and parallel to the *y* axis. For compound (2), the chain becomes skewed giving a zigzag-type arrangement which is even more pronounced in compound (3).

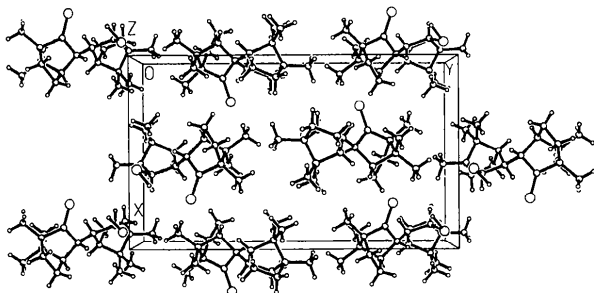


Fig. 2. The packing arrangement in the crystal of compound (1).

Compound (2) (Fig. 3) has an absolute configuration of *1R,2S,3R,6R,13R,16R*. Protons at the C1 and C2 atoms are in *endo* positions relative to the respective norbornane skeleton. The conformation of the C1—C2—C12=C11—S2—S1 ring, described by puckering parameters in polar coordinates ( $Q, \theta, \varphi$ ), is (0.757, 116.16, 102.07). It is thus somewhere between a boat and a half-chair conformation, but closer to a boat. The C2—C12=C11—S2 fragment deviates slightly from planarity; the respective deviations from the plane defined by this fragment are 0.021, -0.049, 0.045 and -0.017 Å. The deviations of the remaining S1 and C1 atoms are -1.331 and -0.445 Å, respectively. The C1—S1—S2—C11 torsion angle is 56.1 (1)° and the S1—S2 distance is 2.056 (1) Å.

The absolute configuration of compound (3) is *1S,3R,6R,11R,13R,16R*. Protons at the C1 and C11 atoms are in

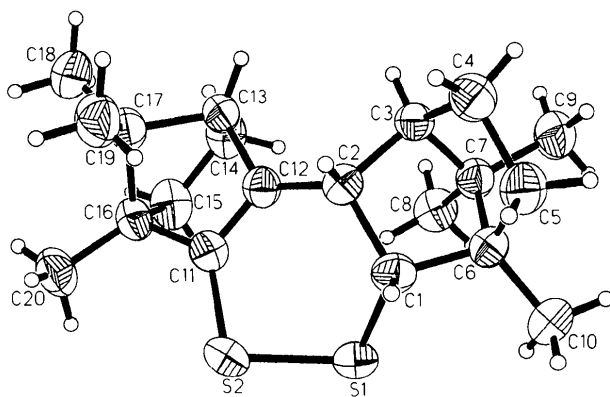


Fig. 3. The molecular structure of compound (2). Displacement ellipsoids are drawn at the 50% probability level.

*endo* and *exo* positions, respectively, with respect to the related norbornane skeleton. The puckering parameters of the C1—C2=C12—C11—S2—S1 ring, expressed in polar coordinates, are (0.779, 115.52, 139.38). Again, the conformation of this ring is between a boat and a half-chair conformation, and closer to a boat. The C1—C2=C12—C11 fragment is planar and the S1 and S2 atoms deviate from the plane defined by this fragment by -1.318 and -0.431 Å, respectively. The C1—S1—S2—C11 torsion angle is 44.9 (2)° and the S1—S2 distance is 2.019 (2) Å.

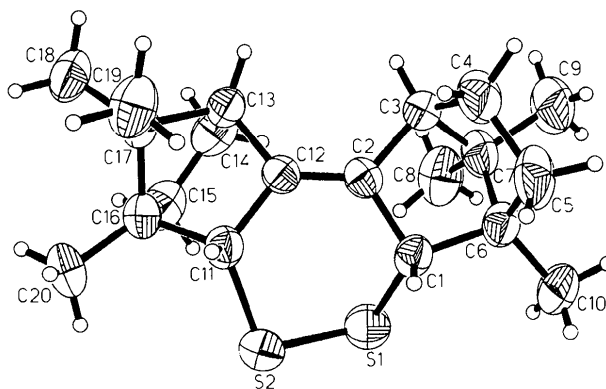


Fig. 4. The molecular structure of compound (3). Displacement ellipsoids are drawn at the 50% probability level.

Although there is some variation observed in the S—S bond lengths of compounds (2), (3) and (4), they all fall within the range obtained from the CSD search (2.005–2.068 Å).

From the values of the torsion angles, compound (3) should be more active than compounds (2) and (4) as an antiviral agent. All these compounds will be subjected to pharmacological screening.

## Experimental

Compound (1) was crystallized from hexane, and compounds (2) and (3) were crystallized from ethanol–water (9:1) solution. Details of the syntheses will be published elsewhere.

### Compound (1)

#### Crystal data

C<sub>20</sub>H<sub>32</sub>S<sub>2</sub>  
*M<sub>r</sub>* = 336.58  
 Orthorhombic  
*P*2<sub>1</sub>2<sub>1</sub>  
*a* = 12.092 (4) Å  
*b* = 20.540 (2) Å  
*c* = 7.772 (2) Å  
*V* = 1930.3 (8) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.158 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

#### Cu *K*α radiation

λ = 1.54178 Å  
 Cell parameters from 25 reflections  
 θ = 18.8–22.9°  
 μ = 2.437 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism  
 0.5 × 0.3 × 0.2 mm  
 Pale yellow

**Data collection**

Rigaku AFC-5R diffractometer with 12 kW rotating-anode generator  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: empirical *via*  $\psi$  scans (North, Phillips & Mathews, 1968)  
 $T_{\min} = 0.556$ ,  $T_{\max} = 0.614$   
 3330 measured reflections  
 2858 independent reflections

**Refinement**

Refinement on  $F^2$   
 $R(F) = 0.0314$   
 $wR(F^2) = 0.0840$   
 $S = 1.026$   
 2858 reflections  
 203 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 0.6175P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = -0.008$

**Compound (2)****Crystal data**

C<sub>20</sub>H<sub>30</sub>S<sub>2</sub>  
 $M_r = 334.56$   
 Orthorhombic  
 $P2_12_12_1$   
 $a = 11.353$  (4) Å  
 $b = 22.289$  (2) Å  
 $c = 7.468$  (1) Å  
 $V = 1889.8$  (7) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.176$  Mg m<sup>-3</sup>  
 $D_m$  not measured

**Data collection**

Rigaku AFC-5R diffractometer with 12 kW rotating-anode generator  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: empirical *via*  $\psi$  scans (North, Phillips & Mathews, 1968)  
 $T_{\min} = 0.511$ ,  $T_{\max} = 0.537$   
 3272 measured reflections  
 2798 independent reflections

**Refinement**

Refinement on  $F^2$   
 $R(F) = 0.0297$   
 $wR(F^2) = 0.0787$   
 $S = 1.055$   
 2798 reflections  
 200 parameters

2663 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.0167$   
 $\theta_{\max} = 59.89^\circ$   
 $h = 0 \rightarrow 13$   
 $k = 0 \rightarrow 23$   
 $l = 0 \rightarrow 8$   
 3 standard reflections plus Friedel equivalents every 150 reflections intensity decay: 4.4%

$\Delta\rho_{\max} = 0.154$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.180$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL93  
 Extinction coefficient: 0.0030 (3)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute configuration: Flack (1983)  
 Flack parameter = 0.00 (2)

Cu  $K\alpha$  radiation  
 $\lambda = 1.54178$  Å  
 Cell parameters from 25 reflections  
 $\theta = 39.6$ – $40.0^\circ$   
 $\mu = 2.489$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism  
 $0.50 \times 0.25 \times 0.25$  mm  
 Colourless

2676 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.0112$   
 $\theta_{\max} = 59.85^\circ$   
 $h = 0 \rightarrow 12$   
 $k = 0 \rightarrow 24$   
 $l = 0 \rightarrow 8$   
 3 standard reflections plus Friedel equivalents every 150 reflections intensity decay: none

$\Delta\rho_{\max} = 0.156$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.119$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL93  
 Extinction coefficient: 0.00108 (15)

H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.6445P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.014$

**Compound (3)****Crystal data**

C<sub>20</sub>H<sub>30</sub>S<sub>2</sub>  
 $M_r = 334.56$   
 Orthorhombic  
 $P2_12_12_1$   
 $a = 12.335$  (1) Å  
 $b = 21.044$  (2) Å  
 $c = 7.293$  (2) Å  
 $V = 1893.1$  (6) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.174$  Mg m<sup>-3</sup>  
 $D_m$  not measured

**Data collection**

Rigaku AFC-5R diffractometer with 12 kW rotating-anode generator  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: empirical *via*  $\psi$  scans (North, Phillips & Mathews, 1968)  
 $T_{\min} = 0.562$ ,  $T_{\max} = 0.608$   
 3320 measured reflections  
 2801 independent reflections

**Refinement**

Refinement on  $F^2$   
 $R(F) = 0.0536$   
 $wR(F^2) = 0.1494$   
 $S = 1.000$   
 2801 reflections  
 200 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 2.6583P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.004$

For all three data sets, data within the volume of a reciprocal space bounded by  $h = 0 \rightarrow h_{\max}$ ,  $k = 0 \rightarrow k_{\max}$ ,  $l = 0 \rightarrow l_{\max}$  and their Friedel equivalents were measured. For all compounds, H atoms were placed in calculated positions and refined using a riding model, with  $U$  equal to  $1.2U_{\text{eq}}$  of the parent atom. For compound (1), the coordinates of the H1 atom were refined.

For all compounds, data collection: *AFC-5R Diffractometer Control Software* (Rigaku Corporation, 1990); cell refinement: *AFC-5R Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structures: *SHELXS90* (Sheldrick, 1990);

Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute configuration: Flack (1983)  
 Flack parameter = 0.01 (2)

Cu  $K\alpha$  radiation  
 $\lambda = 1.54178$  Å  
 Cell parameters from 25 reflections  
 $\theta = 33.6$ – $38.7^\circ$   
 $\mu = 2.484$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism  
 $0.25 \times 0.20 \times 0.20$  mm  
 Colourless

1906 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.0303$   
 $\theta_{\max} = 60.05^\circ$   
 $h = 0 \rightarrow 13$   
 $k = 0 \rightarrow 23$   
 $l = 0 \rightarrow 8$   
 3 standard reflections plus Friedel equivalents every 150 reflections intensity decay: none

$\Delta\rho_{\max} = 0.713$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.239$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL93  
 Extinction coefficient: 0.0005 (3)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute configuration: Flack (1983)  
 Flack parameter = 0.00 (4)

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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*Acta Cryst.* (1997). **C53**, 391–393

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

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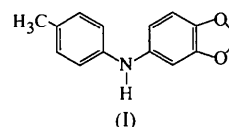
(Received 4 April 1996; accepted 9 October 1996)

## Abstract

The title compound, C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub>, 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<sub>aryl</sub>—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