

2-(*N,N*-Diphenylamino)benzoic acidAnna Boużyk,<sup>a</sup> Antoni Konitz<sup>b</sup> and Jerzy Błażejowski<sup>a\*</sup><sup>a</sup>University of Gdańsk, Faculty of Chemistry, J. Sobieskiego 18, 80-952 Gdańsk, Poland, and <sup>b</sup>Technical University of Gdańsk, Department of Inorganic Chemistry, G. Narutowicza 11/12, 80-952 Gdańsk, Poland  
Correspondence e-mail: bla@chemik.chem.univ.gda.pl

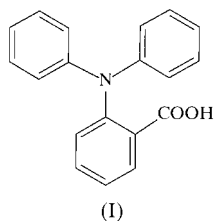
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Shaped like a distorted propeller, molecules of the title compound, C<sub>19</sub>H<sub>15</sub>NO<sub>2</sub>, form centrosymmetric dimers in the crystalline phase in which the carboxy groups are linked through two hydrogen bonds. These dimers are arranged in columns held together *via* dispersive interactions between the phenyl moieties. The N atom and the three surrounding C atoms lie almost in the same plane, which implies that the lone electron pair of the N atom is involved in conjugation with the  $\pi$  systems of the phenyl fragments.

## Comment

Triphenylamine is a unique aromatic amine in which three phenyl substituents are attached to the N atom. The large size of the substituents means that all three C—N—C angles are *ca* 120°, and the N atom and the three adjacent C atoms lie in a single plane (Sobolev *et al.*, 1985). The phenyl substituents surround the N atom, taking up an irregular propeller-like shape (Table 1). For such a structure, one may expect that the lone electron pair of the N atom occupies the *p* orbital perpendicular to the plane formed by the four central atoms and conjugates with the phenyl moieties of the substituents. This lone electron pair is less available to a proton, so the proton affinity of triphenylamine is lower than that of the majority of aromatic or aliphatic amines (Ikuta & Kebarle, 1983). If the phenyl fragments are substituted, the distortion from the regular propeller structure depends on the size and character of the atoms or groups attached. However, the phenyl substituents in tris(2-methoxyphenyl)amine surround the N atom, taking up a regular propeller-like shape (Table 1).



To our knowledge, the structures of more than ten compounds (some are listed in Table 1) originating from triphenylamine have been established so far and none of them contains a

group able to participate in strong hydrogen-bonding interactions. The title compound, (I), contains a carboxy group and it was our intention to explore the extent to which the presence of this group affects the structural and physico-chemical features of the crystalline phase.

In the crystalline phase, a molecule of (I) is shaped like a distorted propeller (Fig. 1), since the phenyl substituents are unequally twisted relative to the plane formed by the N and the three neighbouring C atoms (Tables 1 and 2). Note that the C—N—C angles are almost equal (a total of 359.92°) and the N—C bonds spread almost symmetrically from the N atom (Table 2). This means that the N atom is *sp*<sup>2</sup>-hybridized and the lone electron pair occupies the *p* orbital perpendicular to the plane formed by the four central atoms. This lone electron pair is involved in conjugation with the  $\pi$ -aromatic systems of the benzene rings. As a result, the N—C bonds (mean 1.415 Å) are only *ca* 0.002 Å longer than in aromatic amines and *ca* 0.054 Å shorter than in aliphatic ones (*International Tables for X-ray Crystallography*, 1992, Vol. C, pp. 685–706).

All the atoms making up the carboxy group lie in a plane that is twisted through an angle of 13.7° relative to the benzene ring (Table 2). The distance between the C atom of

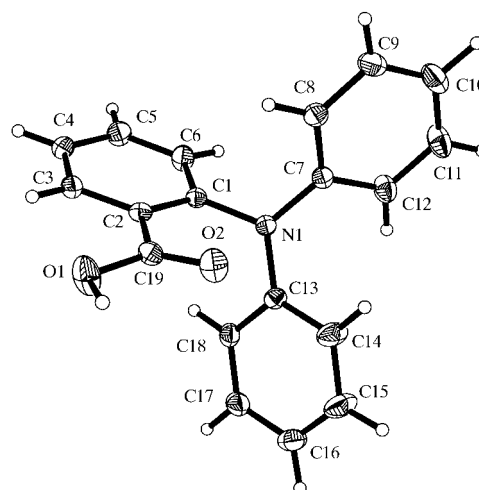


Figure 1

The molecular structure of (I) showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

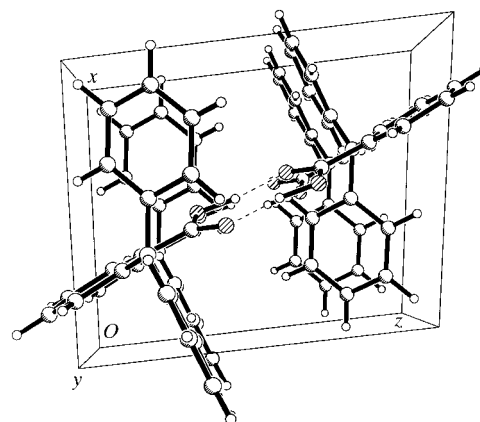


Figure 2

The packing diagram of (I) in the unit cell viewed along the *y* axis. Hydrogen bonds are represented by dashed lines.

the benzene ring and the C atom of the carboxy group is typical for carboxylic acids (*International Tables for X-ray Crystallography*, 1992, Vol. C, pp. 685–706). On the other hand, the O–C distances within this group are almost equal, which suggests that both O atoms are involved in strong hydrogen bonds. Indeed, the arrangement of molecules in the crystalline phase shows that the carboxy groups are bonded *via* a couple of hydrogen bonds (Fig. 2), whose geometry is the same as in the strong bonds (Table 3). The dimers of (I) formed as a result of hydrogen bonding are arranged in the crystal in columns held together *via* dispersive interactions between the phenyl moieties. These unique structural features of (I) explain the ease of formation and the relatively high stability of its crystalline phase.

### Experimental

The title compound was synthesized according to the method described by Goldberg & Nimerovsky (1907). Green crystals of (I) suitable for X-ray investigation were grown from ethyl alcohol.

#### Crystal data

$C_{19}H_{15}NO_2$	$Z = 2$
$M_r = 289.32$	$D_x = 1.282 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.145 (2) \text{ \AA}$	Cell parameters from 50 reflections
$b = 9.427 (2) \text{ \AA}$	$\theta = 6\text{--}13^\circ$
$c = 9.889 (2) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$\alpha = 85.19 (3)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 82.64 (3)^\circ$	Plate, green
$\gamma = 62.45 (3)^\circ$	$0.5 \times 0.3 \times 0.3 \text{ mm}$
$V = 749.3 (3) \text{ \AA}^3$	

#### Data collection

Kuma KM-4 diffractometer	$h = -11 \rightarrow 11$
$\theta/2\theta$ scans	$k = -12 \rightarrow 12$
4376 measured reflections	$l = -13 \rightarrow 0$
4175 independent reflections	3 standard reflections
1581 reflections with $I > 2\sigma(I)$	every 200 reflections
$R_{\text{int}} = 0.036$	intensity decay: 22%
$\theta_{\text{max}} = 30.1^\circ$	

**Table 1**

Selected structural data for triphenylamino derivatives ( $\text{\AA}, ^\circ$ ).

Compound name	Space group	$Z$	Average N–C distance <sup>a</sup>	Angle of inclination <sup>b</sup>			Ref.
				1	2	3	
2-( <i>N,N</i> -Diphenylamino)-benzoic acid	$P\bar{1}$	2	1.415 (3)	64.5	35.8	29.2	(i)
Triphenylamine <sup>c</sup>	$B11b$	16	1.418	39.7	41.4	49.4	(ii)
				38.2	44.6	50.5	
				40.3	41.5	48.0	
				37.0	44.4	49.8	
Tri(4-methylphenyl)amine <sup>d</sup>	$P\bar{1}$	4	1.421	30.7	33.0	61.2	(iii)
				31.3	36.7	58.2	
Tri(2-methoxyphenyl)amine	$Pa3$	8	1.422	44.4	44.4	44.4	(iv)
Tri(2,3,4,5,6-pentachlorophenyl)amine	$A2/a$	4	1.421	50.1	50.1	54.6	(v)
Tri[4-( <i>N-tert</i> -butylamino- <i>N</i> -oxy)phenyl]amine	$Cc$	4	1.421	29.8	34.2	57.2	(vi)

Notes: (a) average distance between the central N atom and the adjacent C atoms; (b) angle between the average plane formed by the central N atom and the adjacent C atoms, and the average plane formed by all C atoms of benzene rings 1, 2 or 3; (c) 16 molecules in the unit cell and four in the independent part of the unit cell; (d) four molecules in the unit cell and two in the independent part of the unit cell. References: (i) this work; (ii) Sobolev *et al.* (1985); (iii) Reynolds & Scaringe (1982); (iv) Müller & Bürgi (1989); (v) Hayes *et al.* (1980); (vi) Itoh *et al.* (1999).

#### Refinement

Refinement on $F^2$	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0699P)^2]$
$wR(F^2) = 0.151$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\text{max}} < 0.001$
4175 reflections	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
259 parameters	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$

**Table 2**

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

N1–C1	1.426 (2)	O1–C19	1.299 (2)
N1–C7	1.409 (2)	O2–C19	1.227 (2)
N1–C13	1.411 (2)		
C1–N1–C7	118.01 (14)	O1–C19–C2	114.72 (18)
C1–N1–C13	118.60 (14)	O2–C19–C2	123.23 (18)
C7–N1–C13	123.31 (15)	O1–C19–O2	121.99 (18)
C19–O1–H1	105.8 (16)		
C1–N1–C7–C8	–36.9 (2)	C2–C1–N1–C13	–65.3 (2)
C7–N1–C13–C14	–31.8 (3)	O2–C19–O1–H1	–3 (2)
C1–C2–C19–O2	–13.7 (3)		

**Table 3**

Hydrogen-bonding geometry ( $\text{\AA}, ^\circ$ ).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O1–H1 $\cdots$ O2 <sup>i</sup>	1.08 (4)	1.59 (4)	2.657 (3)	168 (3)

Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .

No constraints were applied to H atoms. The mean  $C_{\text{ar}}\text{--}H$  distance was 0.97  $\text{\AA}$ . C–H bond lengths were in the range 0.92–1.02  $\text{\AA}$  and their s.u.s did not exceed 0.03  $\text{\AA}$ .

Data collection: *KM-4 Software* (Kuma Diffraction, 1989); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1456). Services for accessing these data are described at the back of the journal.

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