

N,N-Diphenylbenzamide

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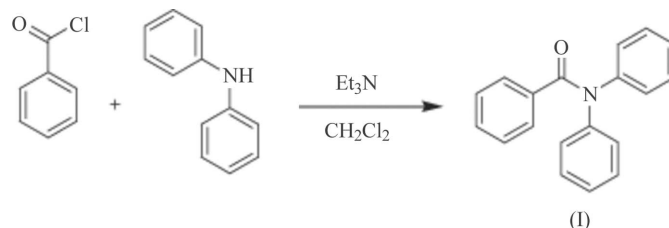
In the title compound, C₁₉H₁₅NO, the neutral molecules are held together in the crystal structure by very weak C—H···O interactions, giving rise to a linear chain-like structure. The structure of the molecule has been optimized using density functional theory at the B3LYP/6-31G(d) level and this is compared with the molecular structure in the solid state. The two structures show significant differences in the relative orientations of the aromatic rings, which is interesting for further supramolecular study. Apart from the crystal structure analysis, powder X-ray diffraction, UV–visible and thermogravimetric analyses of the compound have been carried out.

Comment

The natural occurrence of amide bonds in peptides and proteins makes the amide group important to synthetic chemists (Albericio, 2004; Singh, 2003). Moreover, crystallographic studies of the amide group are as old as the discovery of polymorphism: it was the molecular crystal of benzamide, the simplest of the aromatic amides, where Wöhler & von Liebig (1832) described the existence of polymorphism for the first time. Since this discovery, the literature has recorded a number of reports of structural studies of amides. Of the various different amides, tertiary aromatic amides are of special interest due to the high rotation barrier around the C—N bond, which potentially affords different isomers of amide derivatives (Yamasaki *et al.*, 2006). Structural studies are important in this respect to examine and understand different possible isomers or polymorphs of a molecule. We report here the synthesis, characterization and crystal structure analysis of the title compound, (I). A comparison between the experimental structure and the optimized structure obtained from density functional theory (DFT) calculations is given.

Compound (I) was synthesized by a simple one-pot solution-phase synthetic route, as shown in the scheme. The FT-IR spectrum of (I) shows the carbonyl stretch at 1651 cm⁻¹ and the aromatic C—H stretch at 2943 cm⁻¹. The NMR spectrum recorded in CDCl₃ (400 MHz spectrometer) shows the presence of signals at 7.5 (*d*, 3H, *J* = 8 Hz), 7.3 (*m*, 6H) and

7.16 (*m*, 6H) p.p.m. for the aromatic H atoms. Single crystals of (I) suitable for X-ray analysis were grown from ethanol.



Interestingly, (I) is found to be isomorphous with α,α -*N*-triphenylnitrone, a structural isomer of (I), reported by Brown & Trefonas (1973) (s.u. values = 0.005 Å on distances and 0.03° on angles) and Falshaw *et al.* (1985). However, the two compounds are chemically significantly different.

The asymmetric unit of (I) is shown in Fig. 1. The C13—O1 (carbonyl) bond length is 1.2193 (14) Å, which is comparable with another reported C—O bond length for a tertiary amide (Branca *et al.*, 2008). In the case of α,α -*N*-triphenylnitrone, there is no C—O bond, but an N—O bond of 1.300 Å is present. The N1—C13 bond length in (I) is 1.3734 (16) Å, while the corresponding bond in α,α -*N*-triphenylnitrone is shorter (1.327 Å). The N1 centre in (I) is in an almost planar environment, with bond angles C13—N1—C7 = 123.07 (10)°, C13—N1—C1 = 119.35 (10)° and C1—N1—C7 = 116.86 (9)°. However, in α,α -*N*-triphenylnitrone, the angle around the N atom is significantly different from those in (I) (C—N—O = 125.1°). The shorter bond distance and the different bond angles around the N atom support the contribution of partial π character in the C—N bond of *N,N*-diphenylbenzamide (normal C—N single-bond distance = 1.47 Å).

In general, the C-aryl ring of a tertiary amide remains almost orthogonal to the C=O plane (Branca *et al.*, 2008). However, in the case of (I), the dihedral angle between the mean planes of the benzamide ring and the N1/C13/O1 group is 48.74 (13)°. Moreover, the dihedral angle between the two N-bound phenyl rings is 82.49 (4)°. These observations vary to

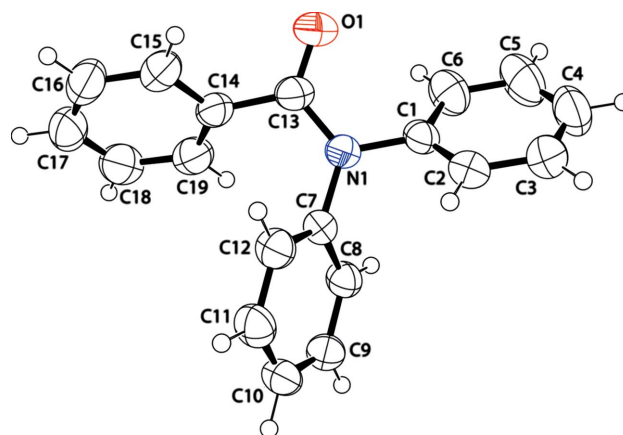


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

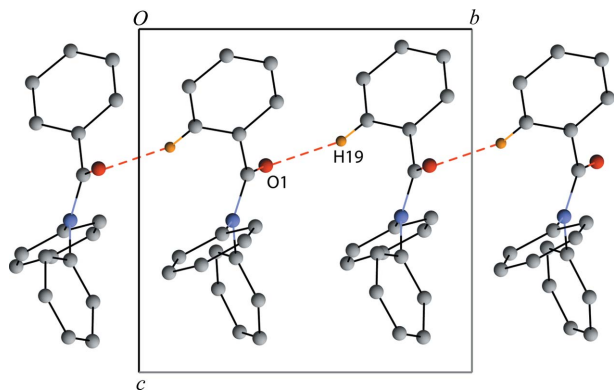


Figure 2
The packing in the structure of (I).

some extent from the optimized structure obtained from DFT calculations (Kohn & Sham, 1965), performed at the B3LYP/6-31G(d) level (Becke, 1993; Lee *et al.*, 1988) using *GAUSSIAN03* (Frisch *et al.*, 2004). Initial atomic coordinates for the DFT calculations were taken from the crystal structure. The DFT calculations predict the C13–O1 and N1–C13 bond lengths to be 1.22 and 1.40 Å, respectively. The average aromatic C–C bond length is calculated to be 1.39 Å, while the experimentally obtained value is 1.37 Å. The calculated bond angles around N1 are C13–N1–C7 = 123.0°, C13–N1–C1 = 118.3° and C1–N1–C7 = 117.4°, and the calculated dihedral angle between the two N-bound phenyl rings is 79.73°. In addition, the calculated dihedral angle between the mean planes of the benzamide ring and the N1/C13/O1 group is 35.29°, which differs significantly from the crystallographically determined value of 48.77 (14)°. These discrepancies between the calculated and crystallographically determined values may be accounted for by solid-state packing effects in the crystal structure of (I), which are not included in the gas-phase DFT structure optimization. Thus, it is clear that, although the bond distances are similar for the two structures, the dihedral angles between the various aromatic rings differ significantly.

These comparisons between the DFT-optimized and experimental structures open up the possibility of polymorphism in *N,N*-diphenylbenzamide arising from the relative orientations of the phenyl rings. Such an observation may attract interest towards a new supramolecular study of *N,N*-diphenylbenzamide and its possible derivatives with substituted phenyl rings.

Apart from these observations, the molecules of (I) in the crystal structure are associated through a very weak C19–H19...O1ⁱ interaction, with H19...O1ⁱ = 2.48 Å and C19–H19...O1ⁱ = 148° [symmetry code: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, z$]. According to the hydrogen-bonding classification provided by Steed & Atwood (2009), this interaction is best described as a very weak electrostatic interaction. This interaction gives the molecule a linear chain-like supramolecular structure propagating along the crystallographic *b* axis, as shown in Fig. 2.

Compound (I) shows an absorption band in the UV region at $\lambda_{\max} = 306$ nm in the solid state, which agrees well with the value of $\lambda_{\max} = 301$ nm predicted by DFT calculation. This

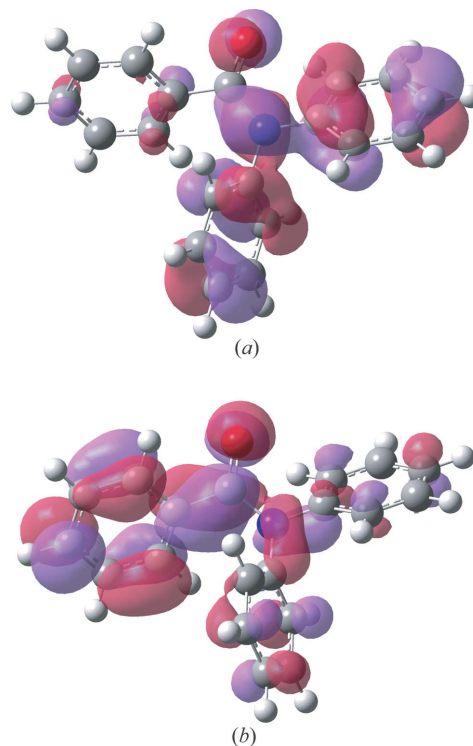


Figure 3
(a) The HOMO and (b) the LUMO of the DFT-optimized structure of (I).

band may be attributed to an intramolecular charge transfer (ICT) from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Such a correlation was recently made by Seidel *et al.* (2009). DFT calculations further reveal that the HOMO is primarily localized on the electron-rich diphenylamino group, while the LUMO is primarily localized on the electron-deficient benzamide group (Fig. 3).

The purity of a chemical sample is an important criterion for spectroscopic analysis. To check the phase purity of the bulk sample of (I), we recorded powder X-ray diffraction data in the 2θ range 5–50°. The experimental powder pattern agrees well with that simulated from single-crystal data (see supplementary material). The thermal stability of the compound was studied under an N₂ atmosphere in the temperature range 298–823 K. The thermogram shows that *N,N*-diphenylbenzamide is stable up to 388 K. Above this temperature it undergoes continuous degradation, with total decomposition of the molecule in the temperature range 388–498 K.

Experimental

Diphenylamine (2.5 g, 0.015 mol) was dissolved in dry dichloromethane (20 ml) and triethylamine (2.07 ml, 0.015 mol) was added. The solution was stirred at 273 K for 15 min and then benzoyl chloride (2.1 g, 0.015 mol) was added dropwise to the stirred solution. The reaction mixture was stirred overnight at room temperature. Water (10 ml) was added to the reaction mixture and the organic layer was collected using a separating funnel. The solvent was then removed under reduced pressure to give the crude product, (I). The product was further purified by recrystallization from ethanol.

Crystal data

$C_{19}H_{15}NO$	$V = 2923.5 (8) \text{ \AA}^3$
$M_r = 273.32$	$Z = 8$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
$a = 17.467 (3) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$b = 9.2050 (16) \text{ \AA}$	$T = 296 \text{ K}$
$c = 18.183 (3) \text{ \AA}$	$0.39 \times 0.32 \times 0.24 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer	32001 measured reflections
Absorption correction: empirical (using intensity measurements) (<i>SADABS</i> ; Sheldrick, 2004)	2852 independent reflections
$T_{\min} = 0.775$, $T_{\max} = 0.822$	2046 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	191 parameters
$wR(F^2) = 0.103$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.15 \text{ e \AA}^{-3}$
2852 reflections	$\Delta\rho_{\text{min}} = -0.12 \text{ e \AA}^{-3}$

The harmonic vibrational analysis at the same level of theory confirmed that the stationary point represented a minimum.

H atoms were placed in calculated positions and refined isotropically using a riding model, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *GAUSS VIEW* (Version 4.1; Frisch *et al.*, 2004); software used to prepare material for publication: *SHELXTL* and *ORTEPIII* (Burnett & Johnson, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3035). Services for accessing these data are described at the back of the journal.

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