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A new polymorph of triphenylmethylamine: the effect of hydrogen bonding

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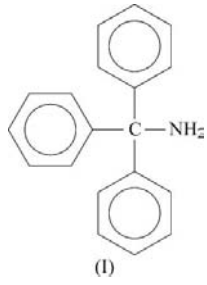
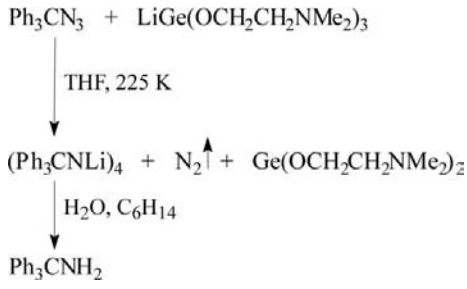
Crystallization of the hexane reaction mixture after treatment of $LiGe(OCH_2CH_2NMe_2)_3$ with Ph_3CN_3 gives rise to a new triclinic (space group $P\overline{1}$) polymorph of triphenylmethylamine, $C_{19}H_{17}N$, (I), containing dimers formed by N—H···N hydrogen bonds, whereas the structure of the known orthorhombic (space group $P2_12_12_1$) polymorph of this compound, (II), consists of isolated molecules. While the dimers in (I) lie across crystallographic inversion centres, the molecules are not truly related by them. The centrosymmetric structure is due to the statistical disordering of the amino H atoms participating in the N—H···N hydrogen-bonding interactions, and thus the inversion centre is superpositional. The conformations and geometric parameters of the molecules in (I) and (II) are very similar. It was found that the polarity of the solvent does not affect the capability of triphenylmethylamine to crystallize in the different polymorphic modifications. The orthorhombic polymorph, (II), is more thermodynamically stable under normal conditions than the triclinic polymorph, (I). The experimental data indicate the absence of a phase transition in the temperature interval 120–293 K. The densities of (I) (1.235 Mg m^{-3}) and (II) (1.231 Mg m^{-3}) at 120 K are practically equal. It would seem that either the kinetic factors or the effects of the other products of the reaction facilitating the hydrogen-bonded dimerization of triphenylmethylamine molecules are the determining factor for the isolation of the triclinic polymorph (I) of triphenylmethylamine.

Comment

The design and preparation of materials with particular properties is one of the principal goals of chemists, physicists and structural biologists. Achieving that goal depends critically on understanding the relationship between the structure of a material and the properties in question. Polymorphic systems are a potential source of detailed information on structure–property relationships in organic solids, since the only variable among polymorphic forms is that of structure, and any variation in properties must therefore be due to structural differences. Moreover, the conditions and techniques required to obtain a particular polymorph, combined with knowledge of the crystal structures, can also provide information on the relative stability of the different structures (Bernstein, 2002).



(I)



On the other hand, the hydrogen bond is a subject that has attracted intense attention due to its importance in a vast number of chemical, biological and materials systems (Steiner, 2002). It has been widely used as a tool for the crystal engineering of organic and organometallic solids (Desiraju & Steiner, 1999; Braga & Grepioni, 2000; Nishio, 2004; Desiraju, 2005).

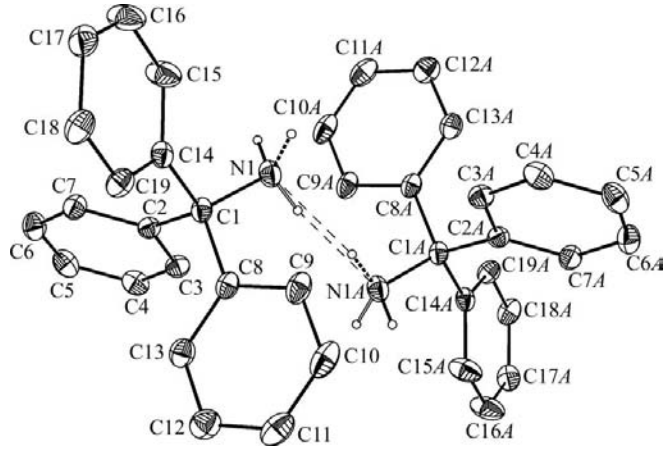


Figure 1
The dimer of (I) formed by intermolecular N—H···N hydrogen bonding, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and only the amino H atoms are shown. The two alternative dispositions of the disordered amino H atoms within the dimer are depicted by heavy dashed and open lines. Thin dashed lines indicate the hydrogen bonds.

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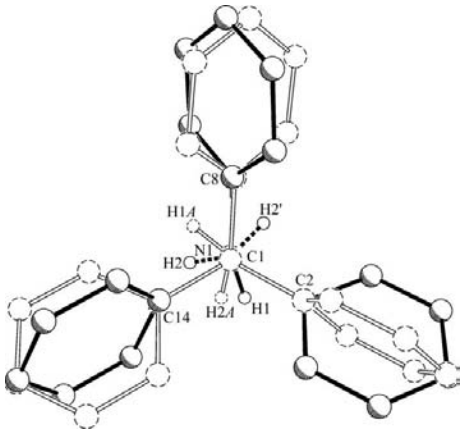

Figure 2
A comparison of the conformations of the molecules of the two polymorphs. The molecules of (I) and (II) are drawn with solid and open lines, respectively.

As a rule, the formation of hydrogen bonds of different types results in a decrease in the total energy of a system and serves as its stabilizing factor. Taking this into consideration, it seemed surprising that triphenylmethylamine, possessing two active H atoms and a hydrogen-bond acceptor, forms only one polymorphic modification without hydrogen bonds (Glidewell & Ferguson, 1994; Clegg & Elsegood, 2005). Therefore, one might expect the existence of another polymorphic modification of this compound, which should contain N—H···N hydrogen bonds. A new triclinic polymorph, (I), of triphenylmethylamine was serendipitously obtained by crystallization of a hexane reaction mixture after treatment of $LiGe(OCH_2CH_2NMe_2)_3$ with Ph_3CN_3 and we report its structure here.

Polymorph (I) crystallizes in the triclinic space group $P\overline{1}$, rather than in the previously known orthorhombic modification of this compound (space group $P2_12_12_1$), (II). The main difference between the two polymorphs is the formation of dimers *via* N—H···N hydrogen bonds in (I) (Fig. 1 and Table 1), whereas (II) consists of isolated molecules. Despite the fact that the dimers lie across crystallographic inversion centres, the molecules are not really connected by them. The centrosymmetric structure is due to the statistical disordering of the amino H atoms participating in the N—H···N hydrogen bonds, and thus the inversion centre is superpositional.

The conformation of the molecules in (I) is such that there is an almost perfect staggering of the N—H and C—Ph bonds. A similar conformation is also characteristic of the molecules in polymorph (II) (Fig. 2). Nevertheless, the mutual disposition of the phenyl rings in the molecules of the two polymorphs is slightly different. In the orthorhombic structure, (II), the phenyl rings have a propeller-like arrangement, with N—C—C—C torsion angles of −12.0 (1), −47.2 (2) and −60.3 (2)°, while in the triclinic structure, (I), the same N—C—C—C torsion angles are −35.2 (2), −39.2 (1) and −53.2 (1)° (Fig. 2).

The aromatic C—C bond lengths in the phenyl rings and the C—Ph bond lengths of the central C atom of (I) fall in the narrow ranges of 1.377 (2)–1.400 (2) and 1.537 (2)–1.541 (2) Å, respectively, and are practically equal to the corresponding values in (II) [1.357 (5)–1.398 (3) and 1.539 (3)–1.541 (3) Å, respectively].

The crystal packings of the molecules in (I) and (II) are topologically similar. They both consist of stacks along the *a* axis and these stacks form layers parallel to the *ab* plane (Figs. 3*a* and 3*b*). However, the arrangements of the molecules relative to each other in neighbouring stacks, and consequently within the layers, differ considerably. In (I), molecules in neighbouring layers are oriented with the amino groups facing each other, which favours the formation of the aforementioned N—H···N hydrogen bonds, while in (II), the amino groups of neighbouring stacks both within and between the layers are oriented away from each other (Figs. 3*c* and 3*d*).

Since the orthorhombic polymorph was obtained by recrystallization from a solution in the polar solvent dichloromethane, while the triclinic polymorph was isolated from a nonpolar hexane solution, we decided to elucidate the influence of solvent polarity on the formation of the different polymophic modifications of triphenylmethylamine. For this purpose, we recrystallized commercially available triphenylmethylamine from solutions in the polar solvents ethanol, diethyl ether and dichloromethane, and the nonpolar solvents hexane, heptane and benzene. It was found that only the orthorhombic modification of triphenylmethylamine is formed from all these solutions at room temperature. Thus, the polarity of solvent does not affect the capability of triphenylmethylamine to crystallize in the different polymorphic modifications. Moreover, the orthorhombic polymorph, (II), is more thermodynamically stable under normal conditions than the triclinic polymorph, (I). It is interesting to note that even the presence of hydrogen bonding in polymorph (I) does not result in its greater stability under ambient conditions compared with polymorph (II).

The possibility of a phase transition from the orthorhombic to the triclinic modification upon cooling was studied by X-ray diffraction analysis in the temperature interval 120–293 K. Our experimental data show that a phase transition does not occur. The densities of the orthorhombic (1.231 Mg m^{-3}) and triclinic (1.235 Mg m^{-3}) modifications at 120 K are practically equal. This result implies that factors other than thermodynamics might be responsible for their formation (Burger & Ramberger, 1979). In the present case, it would seem that either the kinetic factors or the effects of the other products of the reaction facilitating the hydrogen-bonded dimerization of triphenylmethylamine molecules were critical for the isolation of the triclinic polymorph of triphenylmethylamine, (I).

Experimental

An excess (3 ml) of a tetrahydrofuran (THF) solution of Ph_3CN_3 (0.636 g, 2.23 mmol) was added to a THF solution of $LiGe(OCH_2CH_2NMe_2)_3$ (0.5548 g, 1.61 mmol) at 225 K. The liberation of an amount of gas was observed. The reaction mixture was then heated to room temperature for 30 min and allowed to stand overnight. Removal of the solvent by filtration and recrystallization from

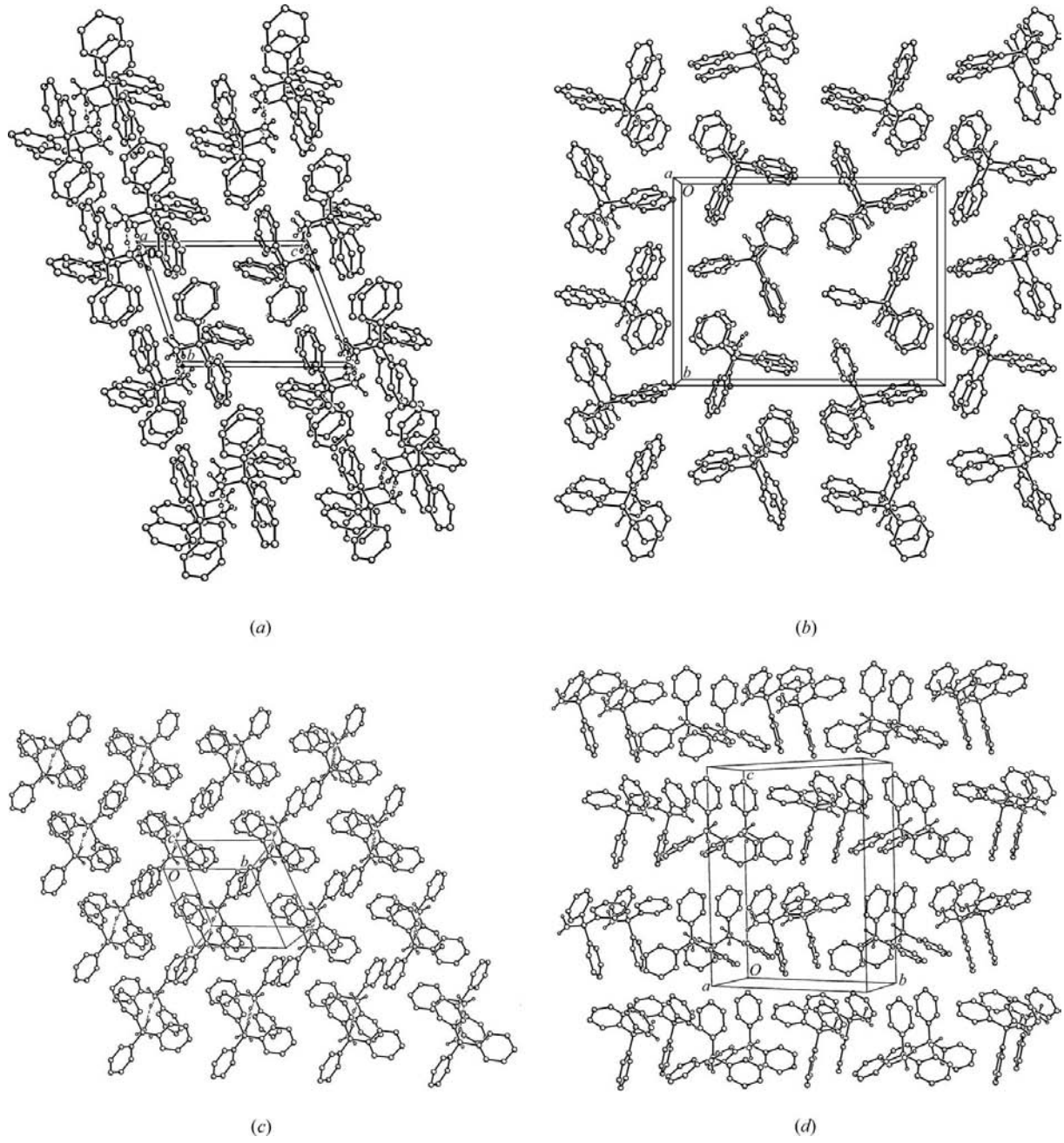

Figure 3
(*a*) A packing diagram of (I) along the *a* axis, indicating the columns of dimers. (*b*) A packing diagram of (II) along the *a* axis, indicating the stacks of molecules. (*c*)/(*d*) Projections of the crystal packing of (I) and (II), respectively, on the C2/C8/C14 plane of the basic molecule, demonstrating the differences in the mutual orientations of neighbouring molecules. Dashed lines in (*c*) indicate hydrogen bonds. H atoms (except for the amino H atoms) have been omitted for clarity.

hexane gave colorless crystals of Ph_3CNH_2, (I) (yield 26%) (see reaction scheme in *Comment*).

Crystal data

$C_{19}H_{17}N$
M_r = 259.34
Triclinic, $P\overline{1}$
a = 8.7255 (8) Å
b = 8.9355 (9) Å
c = 10.6564 (10) Å
α = 68.642 (2)°
β = 81.070 (2)°
γ = 64.314 (2)°
V = 697.32 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 120 (2) K
0.24 × 0.21 × 0.08 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)
T_{min} = 0.984, T_{max} = 0.992
6598 measured reflections
3309 independent reflections
2636 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.146
S = 1.00
3309 reflections
181 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2···N1^{i}	0.93	2.28	3.2069 (19)	173

Symmetry code: (i) $-x, -y+2, -z$.

The amino H atoms were objectively located in a difference Fourier map and refined in the isotropic approximation with fixed positional and displacement parameters [U_{iso}(H) = 1.2U_{eq}(N)]. One of the two amino H atoms is disordered over two sites with equal occupancies. The remaining H atoms were placed in calculated positions and refined in a riding model (C—H = 0.95 Å) with fixed displacement parameters [U_{iso}(H) = 1.2U_{eq}(C)].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3156). Services for accessing these data are described at the back of the journal.

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