

Crystal structure of 4-formyltriphenylamine

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Introduction

The design and synthesis of organic chromophores as nonlinear optical (NLO) materials have attracted much attention in recent years.

They have great potential especially organic NLO materials in the field of optical communications, information processing, frequency doubling and integrated optics, for its advantage of NLO coefficients, greater ease for synthetic design, easy preparation and lower cost. One of the key intermediate is 4-formyltriphenylamine.

NLO chromophore molecules generally have a long conjugated system which contains a electron-donating group on one end and electron-accepting on the other.

It has been shown to improve the thermal stability dramatically using triphenylamine as the donating group.

The popularity of triphenylamine as a building blocks is also developed in many other field, such as solar cells, OLED, two-photo absorption (TPA).

So far there are many more papers refers to the synthesis of 4-formyltriphenylamine. Although there are some different in the synthetic process, the basic idea of them all are under the Vilsmeier-Haack conditions.

Tris(4-formylphenyl)amine (CCDC 197966) and 1,4-bis(bis(4-formyl-phenyl)amino)benzene (CCDC 199659) were not reported but deposited at the Cambridge Crystallographic Data Center as private communication without published in 2002 and 2003, respectively. Another similarly crystal is 4-formylphenyl-bis(4-methylphenyl) amine (CCDC 118423) and reported in 2000.

Although 4-formyltriphenylamine is a very popularity intermediate, the crystal structure was not reported elsewhere.

Here we reported the details of its crystal structure and nineteen C–H \cdots π interactions were found in the crystal.

Experimental

4-formyltriphenylamine was prepared through the Vilsmeier-Haack formylation of triphenylamine according the reported methods [9-11].

The crystal suitable for single-crystal X-ray diffraction was obtained by the slow evaporation of its solution in hexane at room temperature.

Single-crystal X-ray diffraction data of the compound was collected at 293(2) K on an ADSC Quantum210 detector at Beamline 4A MXW of Pohang Light Source.

The crystals evaluation and data collections were done using 0.76999 Å-wavelength radiation with a detector-to-crystal distance of 6.0 cm. Preliminary cell constants and an orientation matrix were determined from 36 sets of frames collected at scan intervals of 5 θ with an exposure time of 1 second per frame. We got basic file from program HKL2000 (Otwinowski & Minor, 1997).

The reflections were successfully indexed by the automated indexing routine of the DENZO program.

Results and discussions

The structure of 4-formyltriphenylamine together with the atom-numbering scheme is illustrated in Fig. 1.

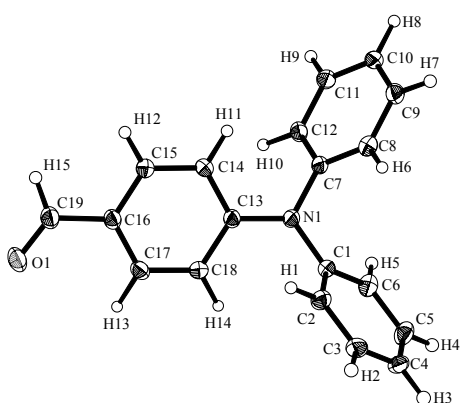


Fig. 1 ORTEP[15] drawing of the title compound with displacement ellipsoids plotted at 50% probability level.

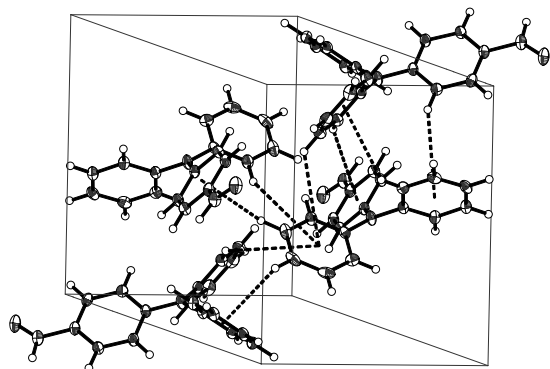


Fig. 2 intermolecular C-H... π interactions in unit cell;

4-formyltriphenylamine crystallizes in a centrosymmetric space group P21/c with four molecules assembled in a unit cell. The bond lengths and angles of the four molecules in the asymmetric unit are almost identical. So the discussion can be limited to one of the molecules. The mean plane of C16-C19-O1 is slightly twisted out of phenyl ring (C13-C18) make a dihedral angle of $3.48(1)^\circ$. The conformation of the three phenyl rings A(C1-C6), B(C7-C12) and C(C13-C18) in one molecule is like the blades of a propeller making N1 a chiral center and the dihedral angle between the three phenyl rings are $80.64(4)^\circ$ (A to B), $69.86(4)^\circ$ (B to C) and $66.06(4)^\circ$ (A to C), respectively. Two right hand and two left hand spiral molecules packing together in unit cell thus make the whole structure achiral. But the three phenyl rings around the central N1 are not arranged

symmetrical with the angles $118.1(1)^\circ$ (C1-N1-C7), $120.0(1)^\circ$ (C7-N1-C13) and $120.8(1)^\circ$ (C13-N1-C1). If the mean plane (C1, C7, C13) was considered as a reference plane, the phenyl rings A, B and C deviated from the reference plane with $47.39(5)^\circ$, $52.07(4)^\circ$ and $28.46(4)^\circ$, respectively. Fig 2. show the unit cell of single crystal structure. In the unit cell, the aldehyde group of four molecular direct outside of the unit cell in four different directions. The $\pi\cdots\pi$ interaction was found between two head-to-head motif molecules. This interaction displays the usual slipped stacking geometry, but with no interacting π system parallel displaced.

Conclusions

There are nineteen C-H... π intermolecular interactions, involving twelve hydrogen atoms and the π electron system of all three phenyl rings. Six of them are intramolecular C-H... π interactions, others are intermolecular C-H... π interactions.

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