# The Low-Temperature Polymorph of Tetramethyldiphosphine-bis(monoborane): Insight into the Stabilization of Different Rotational Isomers in the Solid State

Gerhard Müller and Jörg Brand

Fachbereich Chemie, Universität Konstanz, Universitätsstr. 10, D-78464 Konstanz, Germany

Reprint requests to Prof. Dr. Gerhard Müller. E-mail: gmueller@chemie.uni-konstanz.de

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The low-temperature (LT) polymorph of tetramethyldiphosphine-bis(monoborane), $Me_2(H_3B)P$-$P(BH_3)Me_2$, was obtained by crystallization from diethyl ether at 4 °C. It crystallizes in the monoclinic space group $P2_1/c$, $a$ = 6.464(1), $b$ = 7.605(1), $c$ = 11.867(2) Å, $\beta$ = 119.99(1)° (at 153 K) with 2 molecules per unit cell. This implies that the individual molecules have crystallographic inversion symmetry and a strict *anti* arrangement with respect to the central B-P-P-B skeleton. At 87.6 °C (DTA) the LT polymorph transforms to the high-temperature (HT) modification which contains the *anti* and *gauche* conformers in a 1:2 ratio ($P2_1/c$, $Z$ = 6; H. L. Carrell, J. Donohue, Acta Crystallogr. **B24**, 699 (1968)). This strongly suggests that the *gauche* conformer is higher in energy and stabilized by the crystal packing of the HT modification. The P-P-B angle in the *anti* LT form (113.91(6)°) ascertains the value of the *anti* conformer in the HT form (114.4(6)°) which was found to be significantly different from the *gauche* conformer which centered around 110 °C.

*Key words:* Structure Determination, Polymorphy, Conformer, Thermoanalysis, Phosphine Boranes

## Introduction

Soon after its first synthesis [1] the bis(monoborane) adduct of tetramethyldiphosphine, $Me_2(H_3B)P$-$P(BH_3)$ $Me_2$ (**1**), was recognized to crystallize in two different modifications, a LT "needle-like" polymorph (LT-**1**) and a HT form (HT-**1**) which was referred to as "lump" crystals [2]. While these early investigations were based mainly on microscopic inspection, they showed already that a mixture of the LT and HT polymorphs formed when the compound was synthesized below room temperature [2, 3]. Static heating, preferrably above 112 °C, converted the mixture of polymorphs entirely to HT-**1**, while sublimation under vacuum yielded a mixture of the polymorphs when condensation occurred at low temperatures (typically 0 °C). Condensation at higher temperatures (above room temperature), and especially so at temperatures approaching 100 °C, yielded pure HT-**1** [2]. Clearly, HT-**1** is metastable at room temperature, which was also demonstrated by its structure determination done on single crystals at room temperature [4]. In these early reports it was speculated that the occurrence of two polymorphs might be associated with (or caused by) different molecular conformations, the *anti* rotamer with a B-P-P-B dihedral angle of 180° and the *gauche* rotamer with a dihedral angle near 60° [2]. The crystal structure determination of the HT polymorph surprisingly resulted in the presence of *anti* and *gauche* rotamers in the crystal in a 1:2 ratio [4]. More specifically, the *anti*, D-, and L-*gauche* isomers were present in a ratio of 1:1:1 [5].

As part of our ongoing effort to investigate the ligand capabilities of monoborane adducts of diorganylphosphides, $R_2(BH_3)P^-$ [6], – anionic isoelectronic analogues of triorganylphosphines – we report here on the synthesis of the pure LT polymorph of $Me_2(H_3B)P$-$P(BH_3)Me_2$ and its crystal and molecular structure. Simultaneous thermoanalysis in combination with variable-temperature powder diffraction serves to unambiguously identify the crystalline modifications and their range of existence.

## Results and Discussion

The long-known phosphine borane **1** was synthesized by the unexpected reduction of $SnCl_4$ by $Me_2(BH_3)P^-$ and concomitant oxidation of the anion to the diphosphine in an attempt to prepare phosphine borane complexes of tin (eq. (1)). This proves once more the high reduction potential of borane complexes of phosphides which, taken the other way around, are

| LT-**1** | | HT-**1**[a,b] | | **1** (6-31G*/B3LYP)[b] | |
|---|---|---|---|---|---|
| | | *anti* | *gauche* | *anti* | *gauche* |
| (a) Distances | | | | | |
| P1-P1' | 2.1847(6) | 2.208(5) | 2.202(4) | 2.204 | 2.205 |
| P1-B1 | 1.916(2) | 1.968(16) | 1.927(16)/1.957(17) | 1.987 | 1.991 |
| P1-C1 | 1.803(2) | 1.816(11) | 1.813(12)/1.835(13) | 1.830 | 1.829 |
| P1-C2 | 1.808(2) | 1.831(11) | 1.836(13)/1.833(12) | 1.830 | 1.833 |
| (b) Angles | | | | | |
| P1'-P1-B1 | 113.96(6) | 114.4(6) | 109.7(6)/110.5(6) | 114.8 | 113.4 |
| P1'-P1-C1 | 103.94(5) | 103.2(5) | 105.7(5)/105.9(5) | 103.9 | 104.1 |
| P1'-P1-C2 | 103.50(5) | 104.1(5) | 103.7(5)/103.7(5) | 103.9 | 107.2 |
| B1-P1-C1 | 113.40(8) | 112.0(8) | 115.1(8)/114.4(8) | 114.0 | 114.8 |
| B1-P1-C2 | 114.55(7) | 115.9(7) | 116.1(8)/115.0(8) | 114.0 | 111.7 |
| C1-P1-C2 | 106.40(8) | 106.0(7) | 106.5(7)/105.4(7) | 104.9 | 104.9 |
| (c) Dihedral angles | | | | | |
| B1-P1-P1'-B1' | 180.0 | 180.0 | −59.2(6) | 180.0 | −87.4 |
| B1-P1-P1'-C1' | 56.08(8) | 58.1(6) | 174.7/175.6 | 54.8 | 148.9/148.7 |
| B1-P1-P1'-C2' | −54.95(7) | −52.5(6) | 64.1/63.8 | −54.8 | 38.1/37.9 |
| C1-P1-P1'-C1' | 180.0 | 180.0 | 49.6 | 180.0 | 25.0 |
| C2-P1-P1'-C2' | 180.0 | 180.0 | −172.9 | 180.0 | 163.4 |
| C1-P1-P1'-C2' | 68.97(8) | 69.4(6) | −61.1/−62.2 | 70.5 | −85.8/−85.8 |

Table 1. Selected interatomic distances (Å), angles and dihedral angles (deg.) of LT-**1**, HT-**1**, and DFT geometry of *anti* and *gauche* **1** (RHF/6-31G*//6-31G*/B3LYP). Estimated standard deviations of the crystal structure parameters in units of the last significant figure in parentheses.

[a] Ref. 4; errors of distances and angles as quoted in the original publication; the dihedral angles are calculated from the published coordinates and are reported without errors; [b] atom numbering adapted to that in Fig. 1.

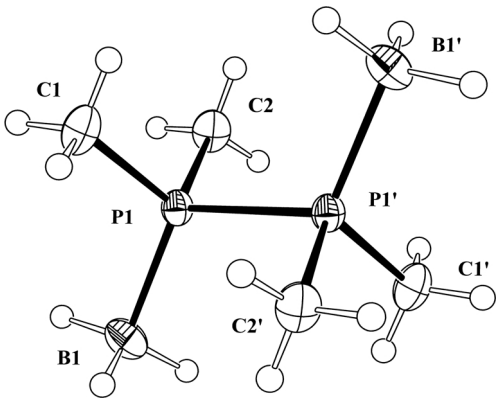


Fig. 1. Perspective view of the molecular structure of LT-**1** in the crystal (ORTEP; displacement ellipsoids at the 50% level, H atoms with arbitrary radii; primed atoms are related to those without a prime by a crystallographic center of inversion: $1-x$, $1-y$, $1-z$).

electron-rich boranates [7]. The synthesis of **1** was carried out in diethyl ether at −20 °C, and the product was recrystallized from ether at 4 °C. The product obtained this way consists entirely of the low-temperature polymorph LT-**1** as was shown by comparison of powder diffraction diagrams taken from various samples of **1** with the powder pattern as calculated on the basis of the single-crystal structure determination [8].

$$4\ Me_2PH\text{-}BH_3 \xrightarrow[Et_2O,\ -80/4\ °C]{1)\ +\ 4\ Li\text{-}nBu,\ -\ 4\ nBuH;\ 2)\ +\ SnCl_4,\ -\ 4\ LiCl,\ -\ Sn} \underset{\mathbf{1}}{2\ Me_2(H_3B)P\text{-}P(BH_3)Me_2} \quad (1)$$

*Crystal and molecular structure*

Single crystals of LT-**1** obtained from ether at 4 °C were monoclinic, space group $P2_1/c$ with 2 molecules in the unit cell. This implies that the individual molecules have crystallographic inversion symmetry and a strict *anti* conformation. Fig. 1 shows the molecular structure, Table 1 contains the most important molecular parameters. Table 1 also summarizes the respective parameters of HT-**1** [4] and those calculated by DFT methods discussed below.

A comparison with the molecular structure of HT-**1** [4] reveals no striking differences, a slight shortening of the respective bond distances in LT-**1** as compared to those in HT-**1** may be attributed to the fact that the HT-**1** data set was taken at room temperature while ours was measured at 153 K. C-P-C angles slightly smaller than the tetrahedral standard, P-P-C angles noticeably smaller, and C-P-B angles larger than the tetrahedral value seem to be typical for monoborane adducts of organodiphosphines. They were also found in $Me_2(BrH_2B)P\text{-}P(BH_2Br)Me_2$ [9]. Probably the most important structural parameter in LT-**1** is the angle P-P-B (113.91(6)°). It compares to the respective angle of $114.4 \pm 0.6$ in *anti* HT-**1** while in *gauche* HT-**1** these angles are noticeably smaller ($109.7 \pm 0.6$ and $110.5 \pm 0.6°$; all errors as quoted in the original publication) [4]. It was speculated that systematic errors in the HT-**1** data set might be responsible for this puzzling discrepancy [4], but our data now suggest that the large P-P-B angle is inherent for *anti*-**1** [10]. It should be noted, however, that in

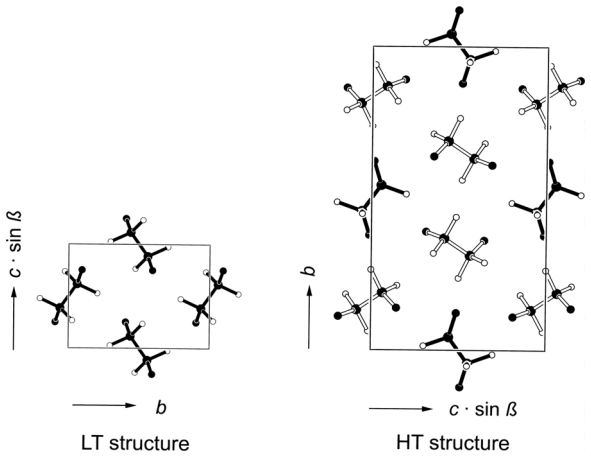


Fig. 2. Projections of the unit cell contents of LT-**1** (left) and HT-**1** (right) onto the *bc* planes (PLATON; P and B atoms are shown as filled circles, C atoms as open circles; *anti* conformers are shown with filled bonds, D- and L-*gauche* conformers of HT-**1** with open bonds).

$Me_2(BrH_2B)P\text{-}P(BH_2Br)Me_2$ (likewise *anti*) the P-P-B angle is only 107.4(2)° [9].

Simple DFT calculations on the 6-31G*/B3LYP level reproduced the geometrical parameters of both rotamers astonishingly well (Table 1) [11]. The most evident discrepancies are between the computational dihedral (torsion) angles of the *gauche* rotamer and those found in the crystal of HT-**1** (Table 1). As the respective parameters show, the computed and found *gauche* geometries differ significantly with respect to the torsion around the central P-P bond. Quite remarkably, the computational P-P-B angles differ only slightly between *anti* and *gauche* rotamers (114.8 *vs.* 113.4°). Both of these values come close to the angles found in the crystalline *anti* rotamers (LT-**1**: 113.96(6); HT-**1**: 114.4(6)°) but are larger than P-P-B in *gauche* HT-**1** (109.7(6)/110.5(6)°). Like the original authors [4] we do not have any clear-cut explanation for this angle difference in HT-**1**. Our computational data suggest that crystal effects (of yet unknown nature) might be responsible for the discrepancy. Clearly, further experimental and especially computational work is needed to clarify this point.

In the crystal individual molecules of LT-**1** pack as shown in Fig. 2. As is immediately evident from projections of the cell contents of both crystal structures onto the *bc* plane (Fig. 2), the incorporation of the *gauche* conformers into the crystals approximately triples the initial LT cell without changing the gross overall packing motif [12]. Only minor changes occur in the relative orientation of the individual molecules with respect to each other. As is also evident from Fig. 2, both crystal structures contain a large number of short intermolecular B-H···H-C contacts which should be favored on electrostatic grounds given the known polarity of the B-H and PC-H bonds: B-H($\delta-$)···H($\delta+$)-CP.

*Thermoanalysis*

In order to assess the stability range of the polymorphs of **1** a simultaneous thermoanalysis (DTA, TG, DTG) was recorded (Fig. 3). A relatively sharp endothermic peak at 87.6 °C (onset at 80.7 °C) in the DTA clearly indicates the phase transition between LT and HT polymorphs. A separate DSC measurement gave $\Delta H = 12.7$ kJ·mol$^{-1}$ for the phase transition. Inspection of the substance in a classical melting apparatus showed no indication of melting at this temperature. This was corroborated by variable-temperature powder diffraction which indicated a transition from one crystalline phase to another. The respective powder patterns matched fairly well (visual inspection) those calculated on the basis of the LT (above) and HT crystal structures [4]. At 130 °C a mass loss indicates beginning decomposition of **1** which is known to give mainly $[Me_2PBH_2]_3$ and less $[Me_2PBH_2]_4$ under concomitant evolution of $H_2$ [2]. In addition, unidentified products presumably with a P-B backbone are formed [2]. At 188.7 °C (onset at 177.5 °C) a broad endothermic peak indicates the melting of the mixture. At this point the mass loss amounts to slightly more than 20%. This thermal behavior agrees remarkably well with the (mostly visual) observations by Burg [2]. In addition to the findings described above in the Introduction, he found that the phase transition proceeded smoothly without melting at temperatures above 100 °C [13]. The melting of the HT phase occurred at 194 °C in Burg's experiments, while heating to 154 °C in a sealed (!) tube did not affect the sample. The latter is in contrast to our measurements which indicate appreciable decomposition already at this temperature (in open vessels). Neither Burg's nor our experiments gave any indication of a melting point at 105 – 106 °C [1, 14].

The DFT calculations on the *anti* and *gauche* rotamers of **1** resulted in the *gauche* isomer being higher in energy by 13.0 kJ·mol$^{-1}$.

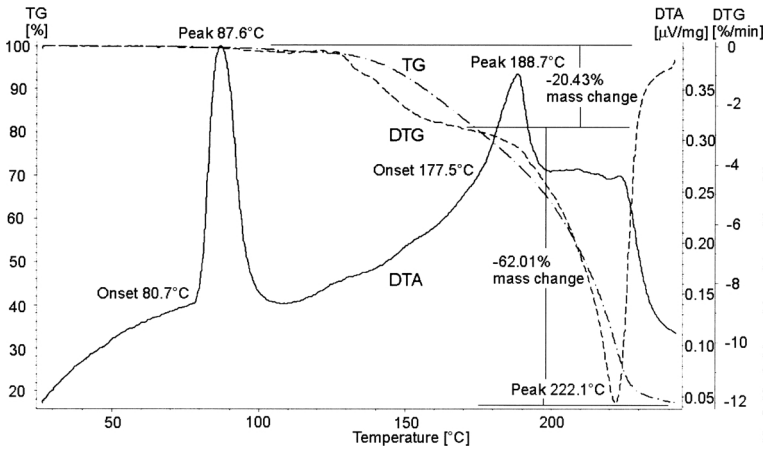


Fig. 3. Simultaneous thermal analysis (DTA, TG, DTG) of **1** between 30 and 240 °C.

## Conclusions

In summary, our experiments confirm that the modification of **1** previously described as needles indeed is the LT polymorph while the "lump" crystals are the HT polymorph. At 87.6 °C the LT form undergoes the phase transition to the HT form. This strongly suggests that the *gauche* conformer existing only in crystals of the HT modification is indeed the less stable rotamer. This is also borne out by the DFT calculations. It should be remembered that $Me_2(H_3B)P\text{-}P(BH_3)Me_2$ (**1**) is isoelectronic with $Me_3Si\text{-}SiMe_3$ where different staggered rotamers are not to be expected. A differentiation between *anti* and *gauche* in **1** solely comes from differently space-filling $P\text{-}BH_3$ *vs.* $P\text{-}CH_3$ groups ($P\text{-}BH_3$ should be less space-filling due to a substantially longer P-B bond). In addition, $Me_2(H_3B)P\text{-}P(BH_3)Me_2$ (**1**) has a more heteropolar charge distribution $B^-\text{-}P^+\text{-}P^+\text{-}B^-$ as compared to C-Si-Si-C. Both factors should favor the observed ground state *anti* conformation of **1** ($P\text{-}BH_3$ staggered between two $P\text{-}CH_3$ groups and a more extended arrangement of the polar skeleton). Thus the original idea that the occurrence of different crystalline modifications might be associated with different conformational isomers is substantiated to the extent that the LT modification contains the ground state *anti* conformer only, while the HT modification contains *anti* and higher-energy *gauche* rotamers in a ratio of 1:2. On the basis of our thermoanalytical data, no further hypothetical modification containing exclusively *gauche* isomers is to be expected at ambient pressure.

The stabilization of higher-energy conformers in crystal lattices is often observed in the case of conformers of simple alkyl groups and of isomers resulting from different relative orientations of alkyl and aryl substituents or lone pairs within one molecule. Also the concept of structure correlation is based to a large extent on the trapping of geometrical non-ground state species in crystalline environments [15, 16]. The prototypal example of biphenyl, which is non-planar in the gas phase, in solution, and in the melt, but planar in the crystal, shall especially be mentioned here [17].

## Experimental Section

All experiments were carried out under exclusion of air and moisture under purified dry argon in standard Schlenk tube glassware or in a glove box. Diethyl ether was dried under argon over sodium-potassium alloy and freshly distilled prior to use. Thermoanalysis: DTA, TG, DTG: Netzsch STA 429, 26.3 mg of **1** in a corund vessel under nitrogen, T range 20 – 280 °C at 5 $°C\cdot min^{-1}$. DSC: Perkin Elmer DSC 7, 1.7 mg of **1**, T range 60 – 120 °C at 10 $°C\cdot min^{-1}$. Variable-temperature X-ray diffraction: Modified Enraf-Nonius Guinier-Simon FR 553 diffractometer, capillary diameter 0.5 mm, Cu-$K_\alpha$ radiation ($\lambda$ = 1.5418 Å), T range 20 – 200 °C at 2 $°C\cdot h^{-1}$. Single crystal X-ray diffraction: Enraf-Nonius CAD4 with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71069 Å).

### *Synthesis of **1***

A solution of 0.74 g (9.75 mmol, ca. 1 ml) of dimethylphosphine borane [6] in 10 ml of diethyl ether was cooled to −80 °C and 3.61 ml of a 2.7 M solution (9.75 mmol) of *n*-butyllithium in hexane (Aldrich) was added slowly with stirring. The reaction mixture was warmed to room temperature and stirring was continued for 1 h resulting in a yellowish solution. After cooling to −20 °C, 0.285 ml

(2.44 mmol) of tin(IV) chloride (Aldrich) was added. A rapid reaction set in, and a yellow precipitate formed which soon darkened. The resulting suspension was stirred for 2 h. Centrifugation resulted in a brown precipitate, which was separated by decantation, and an orange solution. Slow cooling of this solution to 4 °C yielded needle-like crystals. Single crystals suitable for X-ray diffraction were obtained by repeated crystallizations under the same conditions. Crystal yield: *ca.* 20%. $C_4H_{18}B_2P_2$ (149.74): calcd. C 32.1, H 12.1%; found C 31.9, H 12.4%.

*Crystal structure determination*

*Crystal data*: Colorless needle fragment, crystal size = $0.4 \times 0.4 \times 0.4$ mm$^3$, $C_4H_{18}B_2P_2$ (149.74), monoclinic, space group $P2_1/c$ (No. 14), $a$ = 6.464(1), $b$ = 7.605(1), $c$ = 11.867(2) Å, $\beta$ = 119.99(1)°, $V$ = 505.2(2) Å$^3$, $Z$ = 2, $\rho_{\text{calcd}}$ = 0.984 gcm$^{-3}$, $F(000)$ = 164 e, $\mu$(Mo-K$_\alpha$) = 3.53 cm$^{-1}$, $T$ = 153 K. *Data collection and structure refinement: hkl* range: $\pm 7, -9, -14$ to $+7, (\sin\theta/\lambda)_{\max} = 0.617$ Å$^{-1}$, $\theta/2\theta$ scans, $\Delta\omega = 0.5 + 0.35\tan\theta$, 1050 measured reflexions, 996 of which unique, $R_{\text{int}} = 0.025$, 894 reflexions with $I > 2\sigma(I)$, 73 refined parameters, $R(F)$/w$R(F^2)$/GoF ($F^2$): 0.027/0.058/1.08 (all data), $\text{w} = 1/[\sigma^2(F_o^2) + (0.0303 \cdot P)^2 + 0.1127 \cdot P)$, $\text{P} = [\max(F_o^2, 0) + 2F_c^2]/3$, $(\text{shift/error})_{\max} = 0.0$, $\Delta\rho_{\text{fin}}$ (max./min.) = 0.32/−0.2 e/Å$^3$.

A suitable single crystal was mounted under nitrogen on a glass fiber in an inert oil drop at 153(2) K [18]. Exact cell dimensions were determined by refinement of the Bragg angles of 25 selected high-angle reflexions from various parts of reciprocal space carefully centered on the diffractometer ($12.9 < \theta < 24.1°$). Lp and linar decay (−4%) corrections were applied. An absorption correction was not deemed necessary ($T_{\min}$: 0.95, $T_{\max}$: 1.00). All H atoms could be located in difference syntheses. They were refined freely with isotropic displacement parameters. Programs used: DELOS [19], LePage [20] (reduced-cell calculations), HELENA [21] (data reduction), SHELXS/SHELXL-97 [22] (structure solution and refinement), ORTEP-III [23] (structure drawings), and PLATON [24] (structure drawings and molecular geometry) [25].

The *ab initio* and DFT calculations were performed using PC GAMESS version (6.3) of the GAMESS (US) Quantum Chemistry package [26] on a Microsoft Windows XP system.


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[11] The starting geometries were initially optimized with *ab initio* methods on the RHF/6-31-G* level without geometry restrictions. Calculations on the RHF/6-31-G** level did not lead to significantly different results. These geometries were further optimized with DFT methods (6-31-G*/B3LYP).
[12] Upon going from the LT to the HT phase, the cell volume increases from 505.2(2) to 1604.6 Å$^3$, the calculated densitiy diminishes slightly from 0.984 to 0.93 gcm$^{-3}$.
[13] In a typical experiment a mixture of the LT and HT phases was statically heated at 112 °C whereupon the phase transition was observed [2].
[14] The possibility that melting of the LT modification might be observable at 106 °C at a rapid heating rate is improbable, as some of our experiments were done with rates of up to 5 °C·min$^{-1}$.
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