2,5,8-Tri-*tert*-butyl-1,3,4,6,7,9-hexaazaphenalene: Synthesis, Crystal Structure and Calculation of Homolytic N–H Bond Dissociation Enthalpies

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2,5,8-Tri-*tert*-butyl-1,3,4,6,7,9-hexaazaphenalene (**6**) was prepared from diethyl 2-[bis(methylsulfanyl)methylene]malonate (**1**) in four steps. The structure of compound **6** was confirmed by single crystal X-ray diffraction. The phenalene skeleton is nearly planar, and there is no π-π overlap between the hexaazaphenalene rings. A calculation of the homolytic bond dissociation enthalpy (BDE) was performed for compound **6** and its analogs **7** and **8**, and the results were used to explain the different reactivity for these three compounds to form the corresponding radicals.

Key words: Phenalenyl, Hexaazaphenalene, Crystal Structure, Bond Dissociation Enthalpy

Introduction

Phenalenyl chemistry was investigated almost half a century ago [1, 2]. As a highly symmetric (D_{3h}) odd-alternant hydrocarbon π-electronic system with the three redox species of cation, radical and anion [3 – 5], the phenalenyl system plays an important role as a building block in the field of organic multifunctional electronic and magnetic materials [6 – 9]. Azaphenalenyl, as a heteroatomic modification of the phenalenyl system, has also been investigated [10 – 15]. The incorporation of nitrogen atoms into the phenalenyl skeleton was found to substantially affect its electronic structure because of the directionality of lone-pair electrons at the nitrogen sites and the greater electronegativity of nitrogen relative to carbon [16]. Hexaazaphenalenyl, which is expected to bear many resemblances to phenalenyl, is a highly symmetric heterocycle with full nitrogen substitution in all of the α sites of the ring phenalenyl. Suzuki *et. al*. [17] have reported the preparation and single crystal structure of the anion of hexaazaphenalene. It is well known that using the steric effect of bulky groups is an effective strategy to obtain stable radicals, and several phenalenyl radicals bearing the bulky *tert*-butyl group have been isolated as single crystals [10, 13, 18]. Herein, we describe a new *tert*-butyl substituted hexaazaphenalene derivative 2,5,8-tri-*tert*-butyl-1,3,4,6,7,9-hexaazaphenalene (**6**) (Fig. 1), which was prepared by a different synthetic procedure compared to that of hexaazaphenalene. The structure of compound **6** was confirmed by single crystal X-ray diffraction. A calculation of the homolytic bond dissociation enthalpy (BDE) of compound **6** and its analogs **7** and **8** (Fig. 1) has been performed, and the result reveals the reason why compound **6** is difficult to oxidize

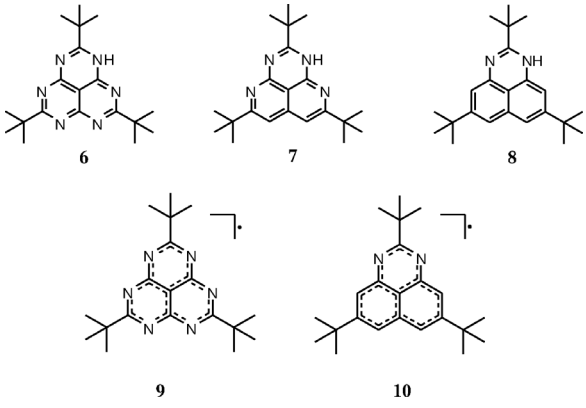
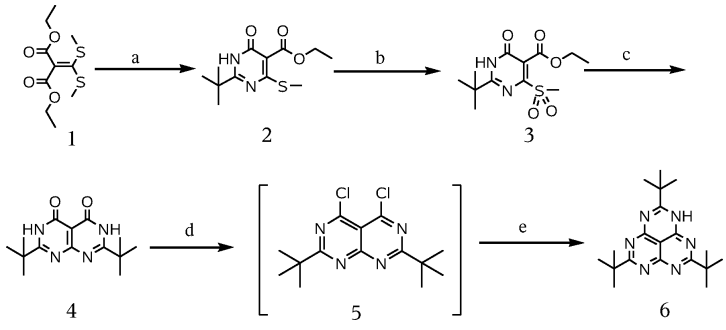


Fig. 1. Chemical structures of **6**, **7**, **8**, **9** and **10**.



a: *t*-Bu-C(=NH)$NH_2 \times$ HCl, $NaOC_2H_5$, C_2H_5OH; b: CH_3COOH, H_2O_2;
c: *t*-Bu-C(=NH)$NH_2 \times$ HCl, $NaOC_2H_5$, $CH_3CH_2OCH_2CH_2OH$;
d: $SOCl_2$, DMF; e: *t*-Bu-C(=NH)$NH_2 \times$ HCl, dioxane K_2CO_3.

Scheme 1. Synthesis of compound **6**.

to its corresponding radical in contrast to its analogous compounds.

Results and Discussion

Synthesis

Because ketene dithioacetals are versatile reagents for the preparation of heterocyclic compounds [19–24], we chose compound **1** as the staring material, which could be easily converted into compound **2** by reacting with *tert*-butylamidine hydrochloride (BAH) in ethanol in the presence of sodium ethoxide as the base. The key intermediate, compound **4**, was synthesized from compound **1** in three steps. At first, we considered that compound **4** could be obtained by reacting compound **2** with BAH, but we were not successful and recovered the starting material **2**. Considering that the nucleophilic displacement of alkylsulfinyl and alkylsulfonyl groups occurs more rapidly than that of an alkylthio group [22, 25], we changed the methylthio group in compound **2** into a methylsulfonyl group to form compound **3** by refluxing **2** in acetic acid in the presence of hydrogen peroxide (30 %). We obtained compound **4** by reacting compound **3** with BAH in ethylene glycol monoethyl ether in the presence of sodium ethoxide as the base. After refluxing compound **4** in an excess of freshly distilled thionyl chloride using DMF as the reaction initiator [26] to form compound **5** and evaporating the excess thionyl chloride, the residue was directly used to react it with BAH in 1,4-dioxane in the presence of potassium carbonate to form the title compound **6** (Scheme 1).

Crystal structure

Single crystals of **6** suitable for X-ray diffraction were obtained by recrystallization from toluene. Crystallographic data of **6** are given in Table 1. The crystal structure of compound **6** is depicted in Fig. 2. Compound **6** crystallizes in the trigonal space group $P3_12_1$ with $Z = 3$. The molecule has crystallographic C_2 (2) symmetry, with the asymmetric unit consisting of one half of the molecule. The two-fold axis passes through atoms C(2), C(3) and C(5) of the molecule. The C–N distances fall in the range of 1.342(4) – 1.373(4) Å. As shown in Fig. 3, the phenalene skeleton is nearly planar, and the maximum deviation from the mean plane of the ring atoms in **6** is 0.075(4) Å for atom N3. The packing of compound **6** in the unit cell is illustrated in Fig. 4. The separation between two adjacent parallel molecules is 7.136 Å. This distance is almost twice as large as the typical van der Waals interaction distance in a C–C π stack [27, 28]. As a consequence there is no

Table 1. Crystal structure data for **6**.

Formula	$C_{19}H_{28}N_6$
M_r	340.47
Crystal size, mm^3	$0.22 \times 0.18 \times 0.16$
Crystal system	trigonal
Space group	$P3_12_1$ (no. 152)
a, Å	10.4574(5)
b, Å	10.4574(5)
c, Å	15.2536(11)
V, $Å^3$	1444.61(14)
Z	3
D_{calcd}, g cm^{-3}	1.174
$\mu(MoK_\alpha)$, cm^{-1}	0.73
F(000), e	552
hkl range	$-13 \le h \le 13$, $-13 \le k \le 13$, $-20 \le l \le 19$
Refl. measured / unique	18366 / 1331
R_{int}	0.079
Param. refined / restraints	147 / 31
$R(F)$ / $wR(F^2)$ (all data)	0.068 / 0.154
GoF (F^2)	1.16
$\Delta\rho_{fin}$ (max/min), e $Å^{-3}$	0.21/−0.22

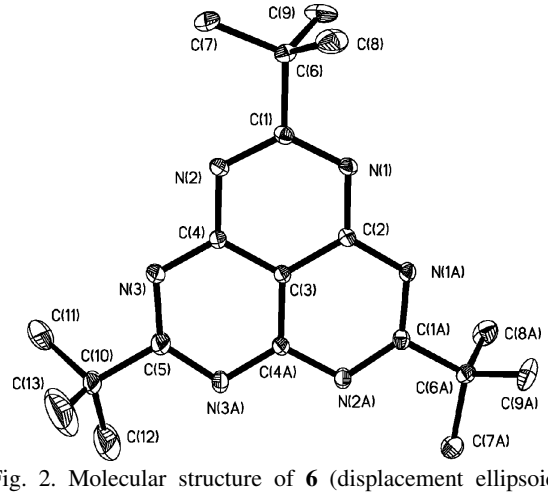


Fig. 2. Molecular structure of **6** (displacement ellipsoids at the 30 % probability level; hydrogen atoms omitted for clarity).

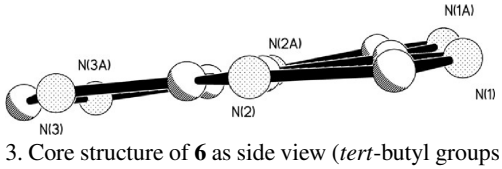


Fig. 3. Core structure of **6** as side view (*tert*-butyl groups and hydrogen atoms omitted for clarity).

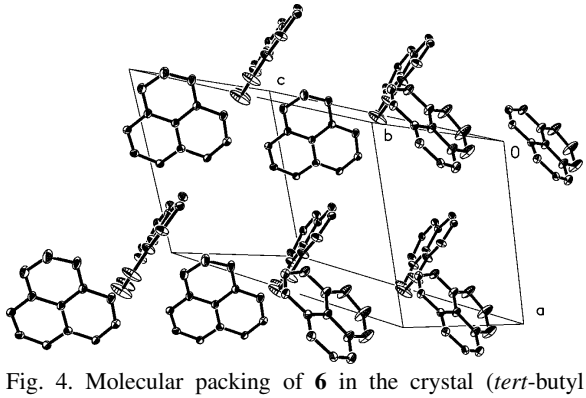


Fig. 4. Molecular packing of **6** in the crystal (*tert*-butyl groups and hydrogen atoms omitted for clarity).

π-π stacking interaction among the hexaazaphenalene rings in the arrays, and the same result has been found in other azaphenalenes [29].

*Bond dissociation enthalpies of the N–H bond for **6**, **7** and **8***

We expected that the reaction of the azaphenalene **6** with oxidants could lead to hydrogen abstraction from the N–H bond to form the stable or persistent phenalenyl-based radical **9** (Fig. 1) as was observed for the transformation **8** → **10** [10]. However, an analogous effort to generate radical **9** by oxidation of **6** with PbO_2 failed [30]. Other oxidation reagents, such as SCl_2 [31] and S_2Cl_2 [32], were also tried, but failed too. One of the most important factors determining the ease of the key step is the N–H bond strength. This prompted us to computationally determine the bond dissociation enthalpies (BDE) for **6**, **7** and **8**.

Table 2. Calculated BDE (N–H) for **6**, **7** and **8** at 298.15 K.

	6	**7**	**8**
BDE, kcal mol^{-1}	71.2	86.0	97.6

The BDEs of the N–H bonds were calculated as the enthalpy change in the gas phase at 298.15 K using

$$A - NH \rightarrow A - N^{\bullet} + H^{\bullet}. \quad (1)$$

The results are shown in Table 2.

As shown in Table 2, the BDE values for compound **6**, **7** and **8** were 97.6, 86.0 and 71.2 kcal mol^{-1}, respectively, which shows that the BDE value of an N–H bond increases with the number of nitrogen atoms incorporated into the phenalene skeleton. The BDE value of compound **6** is about 26.4 kcal mol^{-1} higher than that of compound **8**. This is consistent with the calculated result for compound **7**, which gives a value of BDE (86.0 kcal mol^{-1}) between those of compounds **6** and **8**. Thus, we believe that the high BDE value for compound **6** prevents to extract the hydrogen atom from compound **6** to form the radical **9**. A similar result has been reported for other aza-compounds [33].

Experimental Section

General

Melting points were determined on an RY-I apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC-300 spectrometer with TMS as the internal standard in deuterated solvents. Mass spectra were recorded on a LCQ Advantage spectrometer with ESI source. HRMS were recorded on a VG ZAB-HS mass spectrometer with ESI source. Diethyl 2-[bis(methylsulfanyl)methylene]malonate (**1**) and *tert*-butylamidine hydrochloride (BAH) were prepared according to the literature procedure [34, 35]. All other reagents used were commercially available and purified by standard methods prior to use.

Synthesis

*3,4-Dihydro-4-methylthio-2-tert-butyl-4-oxopyrimidine-5-carboxylic acid ethyl ester (**2**)*

The compound was prepared according to published procedures [36]. To a solution of sodium ethoxide (1.36 g,

20.0 mmol) in absolute ethanol (100 mL) under argon atmosphere, BAH (2.73 g, 20.0 mmol) was added. The mixture was stirred at r. t. for 0.5 h before the addition of diethyl bis(methylthio)methylene malonate (**1**) (5.28 g, 20.0 mmol) and subsequently heated to reflux for 24 h. The resulting solution was concentrated in vacuum to about 10 mL, poured into 100 mL of ice-water and acidified with 10 % aqueous hydrogen chloride. The resulting precipitate was collected by filtration and recrystallized from ethyl acetate to give 3.80 g (14.1 mmol, 70 %) colorless crystals of **2**. M. p. 157 – 159 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.38 (3H, t, J = 3.7 Hz, CH_3), 1.41 (9H, s, *tert*-butyl), 2.52 (3H, s, SCH_3), 4.38 (2H, q, J = 7.0 Hz, CH_2), 11.80 (1H, s, NH). – MS ((+)-ESI): *m/z* (%) = 271 (100) $[M+H]^+$. – HRMS (ESI): *m/z* = 293.0930 (calcd. 293.0930 for $C_{12}H_{18}N_2O_3SNa$, $[M+Na]^+$).

*2-tert-Butyl-4-methylsulfonyl-6-oxopyrimidine-5-carboxylic acid ethyl ester (**3**)*

A mixture of **2** (1.62 g, 6.0 mmol), 3 mL of hydrogen peroxide (30 %) and 15 mL of acetic acid was heated at 60 °C for 6 h. After cooling, the precipitate was collected by filtration and recrystallized from ethyl acetate to give 1.23 g (4.07 mmol, 68 %) of off-white crystals of **3**. M. p. 218 – 220 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.38 (3H, t, J = 7.3 Hz, CH_3), 1.41 (9H, s, *tert*-butyl), 3.21 (3H, s, SO_2CH_3), 4.43 (2H, q, J = 7.1 Hz, CH_2), 11.97 (1H, s, NH). – MS (ESI): *m/z* (%) = 301 (100) $[M–H]^-$. – HRMS ((–)-ESI): *m/z* = 301.0856 (calcd. 301.0864 for $C_{12}H_{17}N_2O_5S$, $[M–H]^-$).

*(3H,6H)-4,5-Dioxo- 2,7-di-tert-butylpyrimido[4,5-d] pyrimidine (**4**)*

To a solution of sodium ethoxide (1.36 g, 20.0 mmol) in 100 mL of ethylene glycol monoethyl ether under argon atmosphere, BAH (2.73 g, 20.0 mmol) was added. The mixture was stirred at r. t. for 0.5 h before the addition of **3** (6.04 g, 20.0 mmol) and then heated to reflux for 24 h. The resulting solution was concentrated in vacuum to about 10 mL, poured into 100 mL of ice-water and acidified with 10 % aqueous hydrogen chloride. The resulting precipitate was collected by filtration, washed thoroughly with water and recrystallized from ethyl acetate to give 3.12 g (11.3 mmol, 60 %) of **4**. M. p. > 300 °C. – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.31 (18H, s, *tert*-butyl), 12.07 (2H, s, NH). – MS (ESI): *m/z* (%) = 275 (100) $[M–H]^-$. – HRMS ((–)-ESI): *m/z* = 275.1511 (calcd. 275.1514 for $C_{14}H_{19}N_4O_2$, $[M–H]^-$).

*2,5,8-Tri-tert-butyl-1,3,4,6,7,9-hexaazaphenalene (**6**)*

Compound **4** (2.40 g, 8.70 mmol) was heated under reflux in 50 mL of freshly distilled thionyl chloride containing dimethylformamide (2 mL) for 12 h. Excess solvent was distilled off, and BAH (2.36 g, 8.70 mmol), potassium carbonate (1.20 g, 8.70 mmol) and 1,4-dioxane (50 mL) were added to the residue. Then the mixture was refluxed for 6 h. After cooling, the reaction mixture was poured into 200 mL of ice-water and acidified with 10 % aqueous hydrogen chloride. The resulting precipitate was collected by filtration, washed with water and recrystallized from toluene to give colorless crystals (1.78 g, 5.22 mmol, 60 %) of **6**. M. p. > 300 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (27H, s, *tert*-butyl), 9.65 (1H, s, NH). – MS (ESI): *m/z* (%) = 341 (100) $[M+H]^+$. – HRMS ((+)-ESI): *m/z* = 341.2441 (calcd. 341.2448 for $C_{19}H_{29}N_6$, $[M+H]^+$).

X-Ray structure determination

A diffraction-quality single crystal of **6** was mounted on a glass fiber in random orientation using epoxy-glue. A Bruker SMART 1000 CCD automatic diffractometer was used for the data collection at T = 113(2) K using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). The structure was solved by Direct Methods using SHELXS-97 [37], and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares calculations on F^2 using the SHELXTL package [38]. The *tert*-butyl group with C(10) as central C atom located near the crystallographic 2-fold axis was disordered in two positions with occupancies of 0.83/0.17. The C–C bond lengths of the disordered group were restrained to 1.54(1) Å, and restraints for atomic displacement parameters of the disordered methyl group were also applied. The C-bound hydrogen atoms were treated as riding on their parent atoms using SHELXTL defaults at 113(2) K, whereas the H atom attached to N(2) was located from a difference Fourier map, and its coordinates were refined with a restrained N–H distance of 0.88(2) Å and U_{iso} = 1.2 U_{eq}(N).

CCDC 680251 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Computational methods

The BDEs of the N–H bonds for compound **6**, **7** and **8** were calculated using *ab initio* quantum mechanical methods with GAUSSIAN 03 [39] on a NKStar Supercomputer. The geometries of the neutral molecules were fully optimized first using the B3LYP method in conjunction with the 6-31+G(d) basis set, and the UB3LYP procedure was used for the geometry optimization of related radicals. Single point energy calculations were then carried out at the B3LYP/6-311++G(2df,2p) level of theory. The enthalpy of a species at 298.15 K was obtained using

$$H(298.15K) = E_0 + ZPE \times 0.9806 + H_{trans} + H_{rot} + H_{vib} + RT. \quad (2)$$

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