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Electronic-spin and columnar crystal structures of stable 2,5,8-tri-*tert*-butyl-1,3-diazaphenalenyl radical

Yasushi Morita [a,*], Kozo Fukui [b], Shuichi Suzuki [a], Takashi Aoki [a], Shigeaki Nakazawa [b], Koichi Tamaki [a], Akira Fuyuhiro [a], Kagetoshi Yamamoto [a], Kazunobu Sato [b], Daisuke Shiomi [b], Akira Naito [c], Takeji Takui [b,*], Kazuhiro Nakasuji [a,*]

[a] *Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*
[b] *Departments of Chemistry and Materials Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan*
[c] *Faculty of Engineering, Yokohama National University, Hodogaya-ku, Yokohama 240-0085, Japan*

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Abstract

1,3-Diazaphenalenyl is a typical example of the isoelectronic mode of heteroatomic modification for phenalenyl. Recently, we have designed and isolated 2,5,8-tri-*tert*-butyl-1,3-diazaphenalenyl (**6**) as the first example of stable azaphenalenyl. For further elucidation of the electronic and solid-state structures of **6**, ^{15}N atoms incorporated 1,3-diazaphenalenyl **7** was designed. New nitration reaction by $K^{15}NO_3$ of 2,7-di-*tert*-butylnaphthalene has enabled us to accomplish effective introduction of ^{15}N atoms and synthesis of **7**. The spin structure of 1,3-($^{15}N_2$)diazaphenalenyl **7** was unequivocally determined by the ratio of the hfcc for ^{14}N and ^{15}N ($A_{14N}/A_{15N} = 0.292/0.409 = 0.714$), which was equal to the ratio of each gyromagnetic ratio ($\gamma_{14N}/\gamma_{15N} = 0.713$). Under an air atmosphere, the radical **7** decomposes slowly, but most of it remains unchanged for weeks. By comparing the spin densities of **7** with those of parent phenalenyl radical **2**, it appears that the spin densities of the 1- and 3-positions decrease appreciably, while those of the 4-, 6-, 7-, and 9-positions increase. The radical **7** forms the *syn*-dimer with gable structure in the crystal, and the dimer stacks in a columnar structure motif.

Keywords: Neutral radical; Diazaphenalenyl; ^{15}N atom; Gyromagnetic ratio; Spin structure; Columnar structure

1. Introduction

Organic neutral radicals have intriguing π-electronic systems, and these features have been widely utilized for basic units of organic materials such as molecule-based magnets or organic metals [1,2]. Phenalenyl (**1**) is a highly symmetric (D_{3h}) odd alternant hydrocarbon π-radical, and Haddon proposed that one-dimensional face-to-face arrangement of phenalenyl was an interesting organic system for realizing molecular conductors based on neutral radical system [3]. For the developments of the phenalenyl chemistry, neutral radicals based on phenalenyl system such as tri-*tert*-butylated phenalenyl (**2**) [4a], perchlorophenalenyl (**3**) [4b,c], zwitterionic bis(phenalenyl) (**4**) [2b,c,4d,e] and 6-oxophenalenoxyl (**5**) [5] have been isolated in the solid state. Furthermore, we have recently designed and synthesized a new neutral radical '2,5,8-tri-*tert*-butyl-1,3-diazaphenalenyl (**6**)' as the first example of stable azaphenaleneyl, which is a typical heteroatomic modification for phenalenyl **2** [6]. In order to clarify the detailed solid-state structure of **6** by the solid-state ^{15}N NMR spectra, we have designed ^{15}N atoms incorporated 1,3-diazaphenalenyl derivative **7** [7]. In this paper, we report on the synthetic method, the detailed spin structure and crystal structure of 1,3-($^{15}N_2$)diazaphenalenyl derivative **7**.

* Corresponding authors. Tel.: +81-6-6850-5393; fax: +81-6-6850-5395.
E-mail address: morita@chem.sci.osaka-u.ac.jp (Y. Morita).

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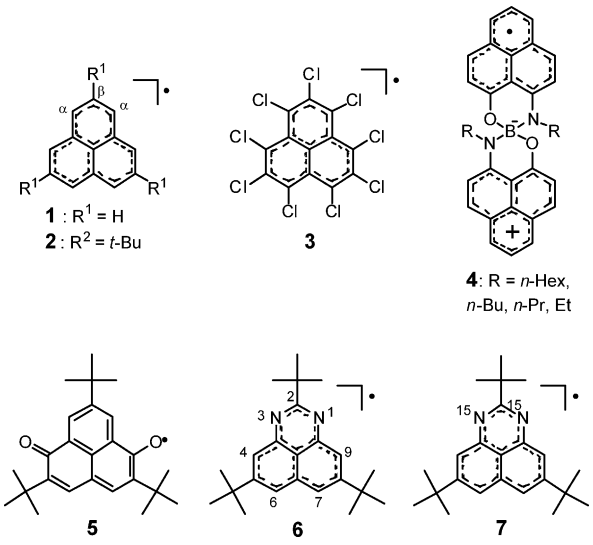


2. Experimental

2.1. Material and methods

All chemicals were reagent grade and used without further purification. 2,7-Di-*tert*-butylnaphthalene (**8**) was prepared from naphthalene according to the reported procedure [8]. Active PbO_2 was prepared by the following method: $Pb(OAc)_4$, (5.05 g, 12.9 mmol) was placed in a 100-ml round-bottomed flask and mixed with H_2O (45 ml). After being stirred at room temperature for 20 min, the resulting solid was filtered and washed with H_2O (50 ml × 2), acetone, and ether, successively. The dark brown solid was dried in vacuo at room temperature for 12 h, to give active PbO_2 (3.10 g, 100%). All reactions requiring anhydrous conditions were performed under argon atmosphere. Toluene was dried and distilled over CaH_2 under argon prior to use. Xylene (mixture of isomers) was dried by the filtration through the Alumina Super I (ICN BIOMEDICALS) column. ^{1}H NMR spectra were recorded on a JEOL EX-270 spectrometer with Me_4Si as an internal standard. EI MS spectra were recorded at 70 eV on a Shimadzu QP-5000. Melting points were recorded with a Yanaco micro melting point apparatus and were uncorrected. The liquid-phase ESR spectra were recorded at 280–290 K on X-band Bruker ESR/ENDOR spectrometer ESP300/350. X-ray crystallographic measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation. Elemental analyses were performed at Analytical Center of Graduate School Science, Osaka University. R_f values on TLC were recorded on E. Merck precoated (0.25 mm) silica gel 60 F_{254}. The plates were sprayed with a solution of 10% phosphomolybdic acid in 95% EtOH and then heated until the spots became clearly visible. Silica gel 60 (100–200 mesh) was used for column chromatography. Deactivated silica gel was prepared by mixing with 6% water, respectively.

2.2. Synthesis of 3,6-di-tert-butyl-1,8-($^{15}N_2$)dinitronaphthalene (9)

2,7-Di-*tert*-butylnaphthalene (**8**) (500 mg, 2.08 mmol), $K^{15}NO_3$ (99 at.% ^{15}N, 425 mg, 4.17 mmol), CH_2Cl_2 (50 ml) and concentrated H_2SO_4 (1 ml) were placed in each four 200-ml round-bottomed flask and stirred at room temperature for 4 h. H_2O (~ 30 ml) was added to each reaction mixture and the resulting solutions extracted with CH_2Cl_2. The organic layers were washed with saturated aqueous $NaHCO_3$, and dried over Na_2SO_4, then filtered and concentrated under reduced pressure. The residual oil was subjected to silica gel column chromatography with a 30:1–10:1 mixture of hexane and ethyl acetate as eluent, to give dinitro derivative **9** (750 mg, 27%) as soft orange powder: m.p. 217–219 °C; TLC R_f 0.38 (5:1 hexane/ethyl acetate); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.46 (s, 18H), 8.06 (d, 2H, $J = 1.8$ Hz), 8.27 (dd, 2H, $J = 1.8$ and 3.0 Hz); *m/z* 332 (M^+, 18%), 317 (M^+—CH_3, 32%), 285 (M^+—$^{15}NO_2$, 100%); *Anal.* Calc. for $C_{18}H_{22}{}^{15}N_2$: C, 65.04; H, 6.67; N, 9.03. Found: C, 64.94; H, 6.62; N, 9.07.

2.3. Synthesis of 1,8-($^{15}N_2$)diamino-3,6-di-tert-butylnaphthalene (10)

3,6-Di-*tert*-butyl-1,8-($^{15}N_2$)dinitronaphthalene (**9**) (591 mg, 1.78 mmol) was placed in a 50-ml round-bottomed flask equipped with reflux condenser and mixed with acetic acid (17 ml) at room temperature. This reaction mixture was stirred at 70 °C for 30 min. To this reaction mixture were added 6 M HCl aq (17 ml) and $SnCl_2 \cdot 2H_2O$ (4.64 g, 20.6 mmol), and stirred for 2 h at 70 °C. After being cooled to room temperature, the resulting white suspension was poured into ice-water (~ 100 g), and then treated with Na_2CO_3 and 2 M NaOH aq, successively, until pH value of the aqueous phase became 9. After extraction with ethyl acetate (50 ml × 2), the organic layer was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl solution, and dried over Na_2SO_4, then filtered and concentrated under reduced pressure. The residual oil was subjected to silica gel column chromatography with a 20:1–3:1 mixture of hexane and ethyl acetate as eluent, to give diamino derivative **10** (292 mg, 60%) as pink powder: mp 103–105 °C; TLC R_f 0.53 (2:1 hexane/ethyl acetate); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.34 (s, 18H), 4.4–4.6 (br, 4H), 6.60 (dd, 2H, $J = 1.8$ and 2.5 Hz), 7,13 (d, 2H, $J =$ 1.8 Hz); EI MS, *m/z* 272 (M^+, 30%).

2.4. Synthesis of 2,5,8-tri-tert-butyl-1,3-($^{15}N_2$)diazaphenalene (**11**)

Diamino derivative **10** (481 mg, 1.77 mmol) was placed in a 50-ml round-bottomed flask equipped with a reflux condenser and mixed with xylene (17 ml), pivalaldehyde (0.25 ml, 2.3 mmol), and 5% Pd/C (114 mg, 3 mol.%). This mixture was refluxed at 160 °C (bath temperature) for 5 h. After being cooled to room temperature, this reaction mixture was subjected to the Na_2SO_4 and celite column to removed the catalyst and water, and rinsed with xylene. The resulting filtrates were concentrated until the total volume became 2/3, and reprecipitated in a refrigerator (0 °C) for 2 days. The generated powder was obtained by the filtration, washed with hexane, and dried in vacuo at room temperature for 1 h, to give diazaphenalene derivative **11** (454 mg, 76%) as a light yellow powder: m.p. 267–268 °C; TLC R_f 0.40 (5:1 hexane/ethyl acetate); EI MS, *m/z* 338 (M^+, 100%).

2.5. Synthesis of 2,5,8-tri-tert-butyl-1,3-($^{15}N_2$)diazaphenalenyl (7)

1,3-Diazaphenalene **11** (150 mg, 0.44 mmol) was placed in a 50-ml Schlenk tube and dissolved with degassed toluene (18 ml). To this mixture was added active PbO_2 (526 mg, 2.2 mmol), and then this mixture was degassed and filled with argon. After being stirred at room temperature for 1 h, the resulting mixture was filtered through the celite column under argon atmosphere, and rinsed with toluene. The filtrates were concentrated in vacuo, to give the crude radical as green solid. A hexane (6.4 ml) solution of this product was degassed, sealed, and recrystallized in a refrigerator (−30 °C) for 5 days. The generated crystals were obtained by the filtration, washed with hexane, successively, and then dried in vacuo at room temperature for 1 h, to give diazaphenalenyl radical **7** (40 mg, 27%) as a green solid: m.p. 164–166 °C (dec); TLC R_f 0.62 (5:1 hexane/ethyl acetate); TLC (alumina) R_f 0.58 (10:1 hexane/ethyl acetate).

2.6. ESR/ENDOR/TRIPLE spectroscopy of the radical 7

A toluene solution of 1,3-($^{15}N_2$)diazaphenalenyl **7** was placed in an ESR tube, and was degassed by freeze-pump-thaw method and the ESR tube was sealed. ESR measurements were performed in a 3×10^{-3} M solution at 280 K. In order to detect the weak ^{13}C satellite peaks, the spectrum was taken for a solution with relatively high concentration. ^1H and ^{15}N ENDOR/TRIPLE measurements were preformed in a 3×10^{-5} M solution at 290 K. The diluted solutions were prepared to enhance ENDOR effects.

2.7. X-ray crystal structure analysis of the radical 7

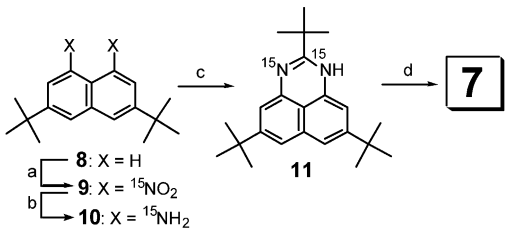
A green crystal of **7** was obtained by recrystallization from *N,N*-dimethylformamide in a sealed tube at room temperature: $C_{46}H_{62}^{15}N_4$, $M_r = 675.00$, crystal dimensions $0.20 \times 0.10 \times 0.08$ mm^3, pale green, Rigaku/MSC Mercury CCD diffractometer, Mo Kα radiation, $T = 23.0$ °C, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.783(1)$, $b = 21.697(2)$, $c = 15.441(2)$ Å, $\beta = 105.957(4)°$, $V = 4117.7(7)$ Å^3, $Z = 4$, $\rho_{calc} = 1.082$ g cm^{-1}, 28 321 reflections collected, 4934 unique intensities reflections observed [$I > 4.00\sigma(I)$], $2\theta_{max} = 55.0°$, structure solution with direct methods (SIR-92) and refinement on F with 483 parameters, R (R_w) = 0.153 (0.396), S (GOF) = 2.23.

3. Results and discussion

3.1. Synthesis of diazaphenalenyl radical 7

The radical precursor, 2,5,8-tri-*tert*-butyl-1,3-($^{15}N_2$)diazaphenalene (**11**) was synthesized from di-*tert*-butylnaphthalene **8** in three steps (Scheme 1). Two nitro groups were effectively introduced to *tert*-butylnaphthalene derivative **8** at 1,8-position with $K^{15}NO_3$ (> 99 at.% ^{15}N) and concentrated H_2SO_4. Dinitro derivative **9** was converted to diamino derivative **10** with $SnCl_2 \cdot 2H_2O$ under acidic condition. Condensation with pivalaldehyde followed by dehydrogenation with Pd/C gave diazaphenalene derivative **11** [9]. The radical **7** was prepared by the treatment of **11** with active PbO_2 in a degassed toluene solution at room temperature and recrystallization from hexane in a sealed tube.

The radical **7** in the solid state is stable in the absence of air. In air the radical decomposes slowly at room temperature, but most of it remains unchanged for weeks. In addition, **7** in solutions of toluene, hexane, *N,N*-dimethylformamide and other several solvents are extremely stable under an inert atmosphere.



Scheme 1. Synthesis of **7**; reagents and conditions: (a) 2 equiv. $K^{15}NO_3$, excess conc H_2SO_4, r.t., 4 h, 27%; (b) 11.5 equiv. $SnCl_2 \cdot 2H_2O$, 6 M HCl aq-AcOH (1:1), 100 °C, 2 h, 60%; (c) 1.3 equiv *t*-BuCHO, 3 mol.% Pd/C, xylene, reflux, 5 h, 76%; (d) 5 equiv. PbO_2, degassed toluene, r.t., 1 h, recrystallized from hexane, 27%.

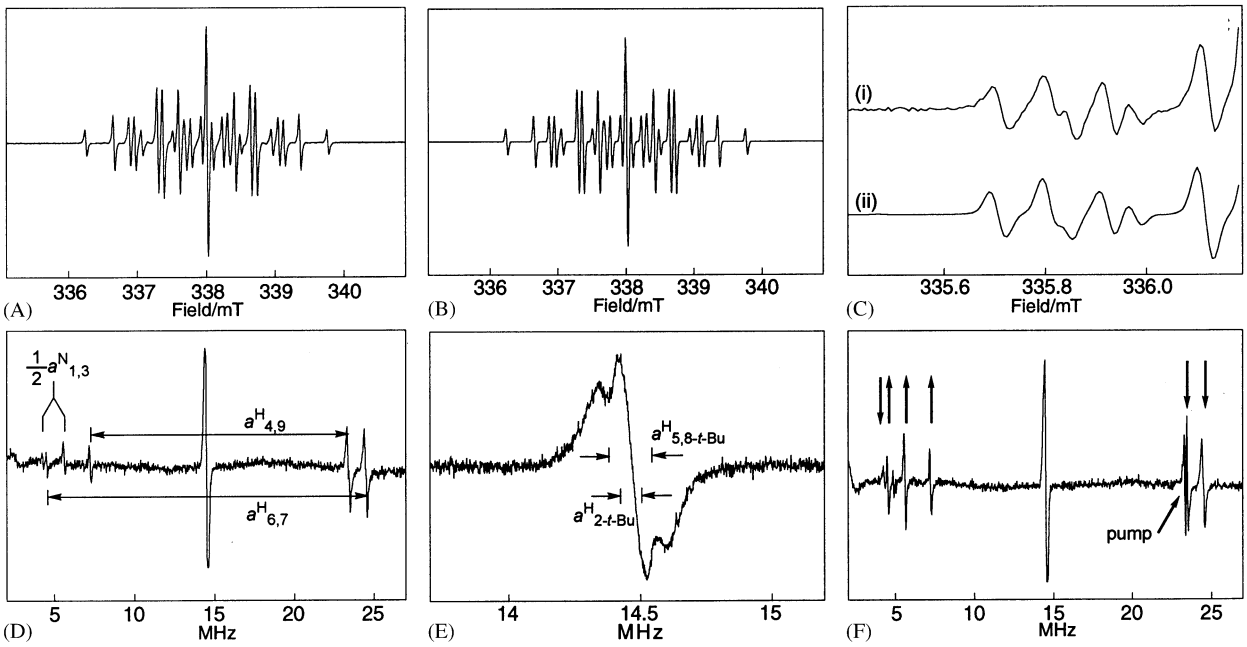


Fig. 1. Observed hyperfine ESR (A, 280 K), simulated (B), the magnification of ESR (C, i; observed, ii; simulated), ^{1}H and ^{15}N ENDOR at 290K (D, 290 K), the magnification of the ENDOR (E) and ^{1}H and ^{15}N TRIPLE (F, pump frequency: 23.37 MHz, 290 K) spectra for **7**; The microwave frequency used for the ESR measurement was 9.4875245 GHz. The observed g-value is 2.0033. Sample concentration of **7** in toluene is 3×10^{-3} M for ESR measurement, 3×10^{-5} M for ^{1}H and ^{15}N ENDOR/TRIPLE measurements.

3.2. ESR/ENDOR/TRIPLE spectroscopy

Fig. 1 shows a well resolved hyperfine ESR spectrum for **7** (Fig. 1(A)), and the simulated one (Fig. 1(B)). The ESR spectrum is explained by assuming two pairs of ^{1}H nuclei, a pair of ^{15}N nuclei. Furthermore, signals due to ^{13}C nuclei with the natural isotropic abundance (1.1%) were distinctly detected (Fig. 1(C)). The ^{1}H and ^{15}N ENDOR spectra show five pairs of lines which were attributed to two kinds of hydrogen atoms on the phenalenyl skeleton, two kinds of t-butyl of hydrogen atoms and a kind of nitrogen atoms (Fig. 1(D and E)). The hyperfine spectral simulation was made based on a set of the isotropic hyperfine coupling constants (hfcc's) obtained by ^{1}H and ^{15}N ENDOR/TRIPLE spectroscopy and ESR satellite signals of ^{13}C nuclei (Fig. 1(C and D)). Relative signs of the coupling constants were determined by ^{1}H and ^{15}N ENDOR/TRIPLE spectroscopy (Fig. 1(F)). All the spin Hamiltonian parameters of hydrogen, nitrogen and carbon atoms for **7** are summarized in Table 1. Assignments of observed hfcc's of **7** were made on the basis of the spin density functional distribution calculated by a local spin density functional theory using Gaussian 98 with the SVWN/6-31G**//SVWN/6-31G*. The structure of 1,3-($^{15}N_2$)diazaphenalenyl was unequivocally determined by the result that the ratio of the hfcc for ^{14}N and ^{15}N ($A_{14N}/A_{15N} = 0.292/0.409 = 0.714$) was equal to the ratio of the corresponding gyromagnetic ratio ($\gamma_{14N}/\gamma_{15N} = 0.713$).

3.3. π-Spin density distribution of the radical 7

Fig. 2 showed the π-spin density distribution of the radical **7** and **2** obtained by the calculations by a local

Table 1
Hfcc's of ^{1}H, ^{13}C and ^{15}N nuclei [a]

a^{H} [mT]				a^{N} [mT]		
4.9	6.7	2-t-Bu [b]	5.8-t-Bu [b]	1.3		
−0.638	−0.715	0.006	0.021	+0.409		
			a^{c} [mT] [c]			
2	4.9	5.8	6.7	10.11	12	13
−0.550	+0.880	−0.820	+1.087	−0.654	−0.885	+0.081

[a] Hfcc's were determined by ^{1}H and ^{15}N ENDOR spectra, ESR satellite signals of ^{13}C nuclei and simulation successfully reproducing the ESR spectra. The relative signs of the hfcc's were determined in terms of ^{1}H-TRIPLE spectroscopy.

[b] The sign was experimentally unknown.

[c] Assignments of the relative signs of the hfcc's were based on DFT calculation using Gaussian 98 with the SVWN/6-31G**//SVWN/6-31G*.

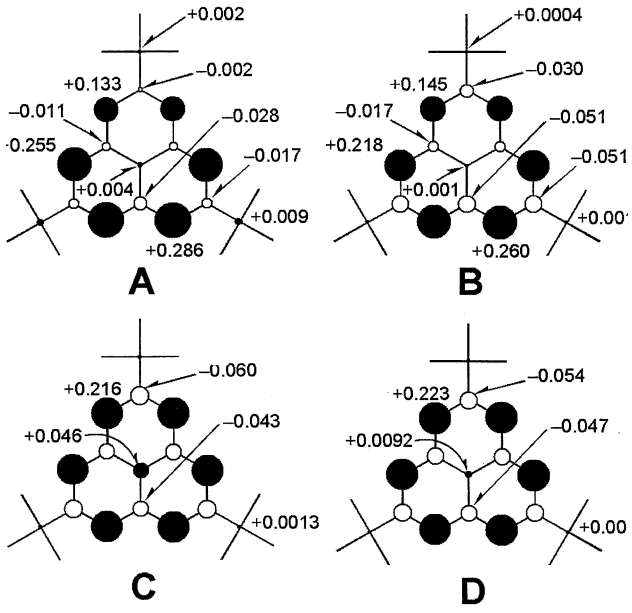


Fig. 2. Experimentally determined π-spin density distributions of the radical **7** (A) and **2** (C), and theoretically calculated π-spin density distributions of **7** (B) and **2** (D) by DFT method using Gaussian 98 (SVWN/6-31G**//SVWN/6-31G*). The vacant and filled circles denote negative and positive spin densities, respectively.

spin density functional theory (Fig. 2(B and D)) and by the experiments with the help of McConnell, Heller–McConnell and Fraenkel–Karplus equations (Fig. 2(A and C)). The experimentally obtained π-spin density distributions of **7** and **2** are in agreement with the theoretical obtained ones. It appears that a robust π-spin polarization similar to the parent phenalenyl **2** is maintained in **7**. By comparing the spin densities of **2** with those of **7**, it turns out that the deviation from C_3-symmetric spin distribution was observed and the spin densities on the ^{15}N atoms decrease, while those of the 4-, 6-, 7- and 9-positions increase.

3.4. X-ray crystal structure of the radical 7

The crystal structure of **7** was shown in Fig. 3. The molecule forms *syn*-dimeric pairs with gable structure in a staggered arrangement of *t*-butyl groups to avoid steric repulsion (Fig. 3(A and B)). In such an arrangement, effective maximum overlaps are expected between the α-carbon atoms having a large coefficient in the singly occupied molecular orbital. The dimer structure of **7** is similar to that of the parent phenalenyl **2**. The distances in the dimeric pair of **7** range from 2.15 to 3.79 Å, while those in the pancake-type stacking of symmetric pure π-dimer structure for **2** range from 3.20 to

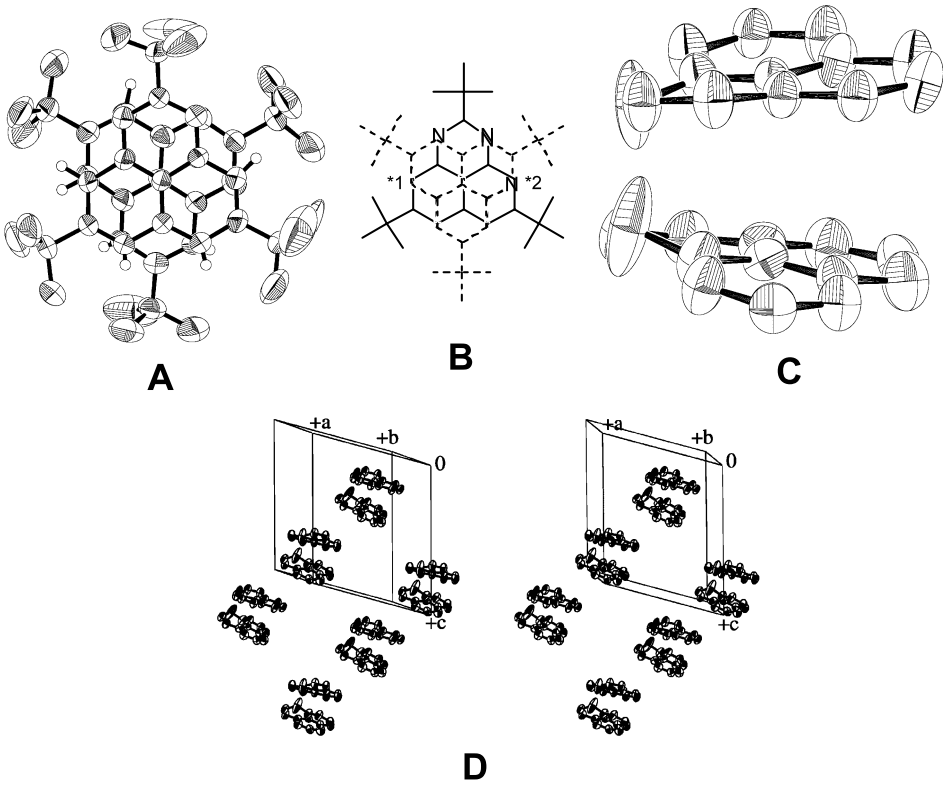


Fig. 3. ORTEP views of the gable *syn*-dimer of **7**. Top view (A) and a schematic representation (B); the nitrogen sites are located in terms of the most probable face-to-face arrangement; *1: the shortest C–C distance and *2: the longest distance between the α-carbon and nitrogen sites. (C) Side view; the *t*-butyl groups are omitted for clarity. (D) Crystal packing of the dimer of **7**; the columnar structure motif is formed. The *t*-butyl groups are omitted for clarity.

3.32 Å (Fig. 3(C)). The gable *syn*-dimer structure for **7** and asymmetric bonding nature formed in the dimer are induced by symmetry-breaking incorporation of nitrogen atoms at the 1- and 3- positions. In the *syn*-dimeric arrangement for **7** effective overlaps occur between the α-carbon sites with largest and next-largest spin densities, and result in the shortest C–C distance in the gable *syn*-dimer structure. The dimer stacks in a columnar structure motif for **7** (Fig. 3(D)), which is important in the organic metals and conducting materials.

4. Summary

The 1,3-($^{15}N_2$)diazaphenalenyl derivative **7** was synthesized and studied by solution cw-ESR, ENDOR/TRIPLE spectroscopies. The agreement between the ratio of the hfcc for ^{14}N and ^{15}N ($A_{14N}/A_{15N} = 0.292/0.409 = 0.714$) and the ratio of the corresponding gyromagnetic ratio ($\gamma_{14N}/\gamma_{15N} = 0.713$) gave a precise picture for the spin structure of 1,3-diazaphenalenyl. The *syn*-dimer with gable structure of **7** and the dimer stacks in a columnar structure motif were determined by an X-ray structure analysis. The further studies of the dimer structure by solid-state CP/MAS ^{15}N NMR and of the synthesis of other azaphenalenyl derivatives are under way.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 183912 (**7**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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