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Synthesis and Crystal Structure of 3-(1,1,1,3,3,3-Hexamethyl-disilazan-2-yl)-1-phenyl-1*H*-indene-2-carbonitrile

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The crystal structure of 3-(1,1,1,3,3,3-hexamethyl-disilazan-2-yl)-1-phenyl-1*H*-indene-2-carbonitrile has been determined by X-ray diffraction method. The crystal is orthorhombic with space group $P2_12_12_1$, a = 8.6317(2) Å, b = 14.8822(3) Å, c = 17.5719(3) Å, V = 2257.26(8) Å^3, Z = 4, and R_1 = 0.047, wR_2 = 0.129 for 2016 observed reflections (I > 2.00σ(I)). The mean plane of indene is almost perpendicular to the phenyl ring attached at chloro atom, the dihedral angling being 84.4(1)º. In the crystal packing, the molecules are stabilized by C-H···π and C-H···N interactions.

Key Words: Indene, Disilylation, Samarium, Crystal structure.

INTRODUCTION

As important synthetic intermediates, the use of indenes have been widely exploited in pharmaceutics, catalysts, metal complexes, polymer chemistry and the syntheses of natural products[1]. However, in most cases, the formation of indene skeleton requires tedious operational procedure and relatively harsh reaction conditions. Recently, it was found that metallic samarium exhibited some extraordinary capabilities when DMF was used as reaction medium instead of traditional THF in our investigations on the applications of metallic samarium in organic synthesis[2]. We now report the crystal structure of the 3-(1,1,1,3,3,3-hexamethyl-disilazan-2-yl)-1-phenyl-1H-indene-2-carbonitrile, which containing indene core, synthesized by an intramolecular cyclization and disilylation of 1,1-dicyano-2,2-diarylethenes promoted by samarium/trimethylsilyl chloride in DMF. Since knowledge of the molecular and crystal structure of the present compound was considered useful for understanding the mechanism of the cyclization, the X-ray crystallographic study was carried out.

EXPERIMENTAL

Synthesis of 3-(1,1,1,3,3,3-hexamethyl-disilazan-2-yl)-1-phenyl-1*H*-indene-2-carbonitrile: To a mixture of samarium powder (2 mmol), 1,1-dicyano-2,2-diphenylethene (2 mmol) in anhydrous DMF (10 mL), trimethylsilyl chloride (TMSCl, 5 mmol, freshly distilled) was added at room temperature with magnetic stirring under a nitrogen atmosphere. The resulting solution turned brown within 10 min and an exothermic reaction was observed. After the completion of the reaction (40 min), a routine workup of the reaction mixture followed by column chromatography afforded the present compound in 87% yield. Anal. % $C_{22}H_{28}N_2Si_2$ Calcd.: C 70.16, H 7.49, N 7.44. Found: C 70.34, H 7.50, N 7.42, IR (KBr, cm^{-1}): 3065, 2956, 2207, 1587, 1557, 1498; δ_H(DMSO-d_6): 7.29 - 7.49 (6H, m), 7.21 - 7.23 (1H, m), 7.12 - 7.13 (2H, m), 5.13 (1H, s), 0.22 (9H, s), 0.19 (9H, s); ^{13}C NMR δ($CDCl_3$): 161.9, 144.9, 140.7, 134.8, 126.82, 126.80, 125.8, 125.5, 125.4, 122.3 119.3, 115.1, 111.1, 52.2, 0.21; m/z (%) : 377 (M^+ + 1, 5.09), 376 (M^+, 13.69), 361 (31.27), 303 (3.33), 288 (2.38), 287 (4.19), 77 (2.55), 73 (100). The single crystals suitable for X-ray analysis were obtained by recrystallization of the product from petroleum ether.

Crystallographic Study: A colorless chunk crystal of $C_{22}H_{28}N_2Si_2$ having approximate dimensions of 0.48 × 0.41 × 0.39 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID Imaging Plate area detector with graphite monochromated MoK_α radiation. The data were collected at a temperature of 23 ± 1°C to a maximum 2θ value of 54.8°. A sweep of data was done using α scans with formed of 5° oscillations. Of the 20600 reflections that were collected, 2894 were unique (R_{int} = 0.034); equivalent reflections were merged. The linear absorption coefficient, for Mo-Kα radiation is 1.65 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.90 to 1.07. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR97)[3] and expanded using Fourier techniques (DIRDIF99)[4]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were seted by calculation and refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 2016 observed reflections and 264 variable parameters and converged (largest parameter shift was 0.00 times) with unweighted and weighted agreement factors of $R_1 = 0.047$ and $wR_2 = [(w(Fo^2 - Fc^2)^2)/w(Fo^2)^2]^{1/2} = 0.129$. The standard deviation of an observation of unit weight was 1.01. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.21 and -0.20 $e^-/Å^3$, respectively. The flack parameter[5] is -0.1(3) and the friedel pairs is 0. Neutral atom scattering factors were taken from Cromer and Waber[6]. All calculations were performed using the crystal structure crystallographic software package[7,8].

RESULTS AND DISCUSSION

Selected bond lengths and angles are presented in Table-1. The hydrogen-bonding interaction distances are listed in Table-2. Fig. 1 shows the molecular structure of the present compound. Packing diagram of the present compound molecules in a unit cell is shown in Fig. 2.

TABLE-1
SELECTED BOND LENGTHS (Å) AND ANGLES (°)
FOR THE 3-(1,1,1,3,3,3-HEXAMETHYL-DISILAZAN-2-YL)-1-PHENYL-1H-INDENE-2-CARBONITRILE

Si(1)-N(2)	1.739(3)	Si(2)-C(14)	1.833(6)
Si(1)-C(11)	1.850(6)	Si(2)-C(15)	1.859(6)
Si(1)-C(12)	1.828(7)	Si(2)-C(16)	1.825(7)
Si(1)-C(13)	1.870(7)	N(1)-C(10)	1.145(6)
Si(2)-N(2)	1.763(3)	N(2)-C(8)	1.428(4)
Si(1)-N(2)-Si(2)	126.2(2)	Si(2)-N(2)-C(8)	115.5(2)
Si(1)-N(2)-C(8)	118.2(2)	C(16)-Si(2)-N(2)	111.3(3)
C(11)-Si(1)-N(2)	108.6(2)	C(14)-Si(2)-N(2)	111.4(2)
C(12)-Si(1)-N(2)	111.2(3)	C(15)-Si(2)-N(2)	109.4(2)
C(13)-Si(1)-N(2)	110.8(3)	C(16)-Si(2)-C(14)	108.9(4)
C(12)-Si(1)-C(11)	107.1(3)	C(15)-Si(2)-C(14)	106.1(3)
C(13)-Si(1)-C(11)	109.6(4)	C(16)-Si(2)-C(15)	109.5(4)
C(13)-Si(1)-C(12)	109.5(3)		

TABLE-2
HYDROGEN-BONDING GEOMETRY (Å, °)

D-H···A	D-H	H···A	D···A	D-H···A
C(1)-H(1)…Cg(3)	1.020(3)	2.737	3.717	161
C(15) -H(19)…N(1)	1.020(6)	2.626(5)	3.642(5)	174.0(5)

* Symmetry codes: (i): -1/2+x,1/2-y,1-z(ii):1-x,-1/2+y,1/2-z

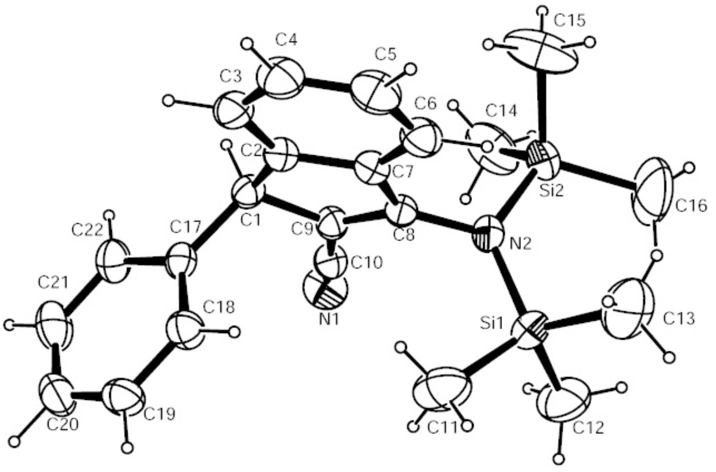

Fig. 1. Structure of the present compound with 30 % probability displacement ellipsoids

In the nonplanar molecule, all bond lengths and angles are within normal ranges[9]. The indene moiety is essentially planar, with a dihedral angle of 1.5(1)° between the C2-C7 ring and its fused five-membered ring. While this mean plane is almost perpendicular to the phenyl ring attached at C1 atom, the dihedral angling being 84.4(1)°. In the crystal packing, the molecules are stabilized by C-H···π and C-H···N interactions.

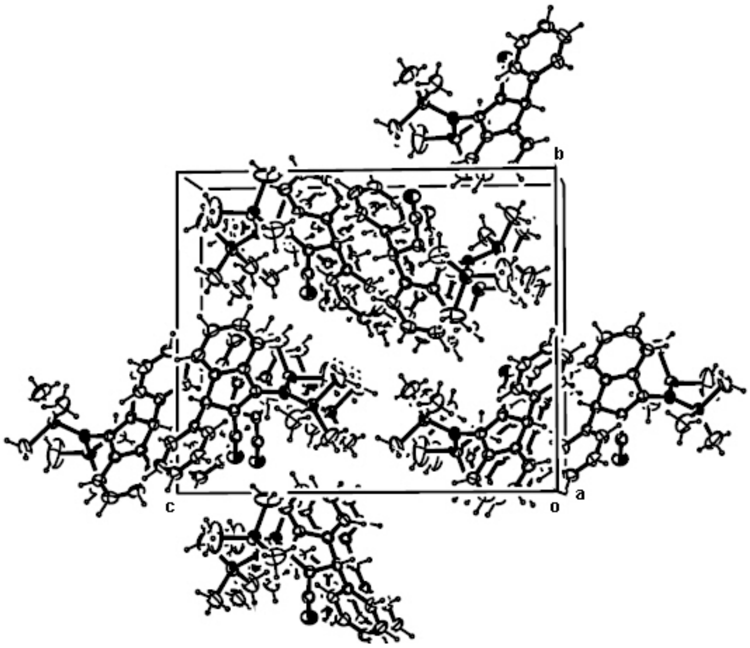

Fig. 2. Molecular packing of 3-(1,1,1,3,3,3-hexamethyl-disilazan-2-yl)-1-phenyl-1H-indene-2-carbonitrile

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