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Structure of Potassium Hexamethyldisilazide Toluene Solvate

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Abstract. $K[C_6H_{18}NSi_2].C_7H_8$, $M_r = 291{\cdot}62$, monoclinic, $C2/c$, $a = 13{\cdot}213\ (5)$, $b = 17{\cdot}077\ (4)$, $c = 15{\cdot}796\ (4)$ Å, $\beta = 95{\cdot}66\ (2)°$, $V = 3546{\cdot}8\ (1{\cdot}2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}09$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 4{\cdot}08$ cm^{-1}, $F(000) = 1264$, $T \sim 173$ K. Final $R = 0{\cdot}045$ for 2062 unique observed reflections. The compound was found to be a dimeric aggregate, the core of which consists of a nearly planar K—N—K—N four-membered ring. The crystallization solvent, toluene, co-crystallizes with the dimer but is not coordinated. Bond lengths and angles are in agreement with those of the monomeric dioxane-solvated compound.

Introduction. The title compound is widely utilized as a base in the formation of kinetic enolate anions. Preparation of the material has been described by Wannagat & Niederprüim (1961). It is commercially available as a toluene solution from several sources (Callery Chemical Co. & Aldrich Chemical Co.). An X-ray crystal-structure determination of the dioxane solvate of this substance has been reported (Domingos & Sheldrick, 1974). Owing to our observation of a difference in reactivity of the differently solvated potassium amide base, it seemed reasonable to undertake the X-ray crystal-structure determination of the toluene solvate.

Experimental. Clear colorless crystal of the potassium amide toluene solvate, prepared by refluxing hexamethyldisilazane with potassium hydride in toluene followed by recrystallization from toluene ($0{\cdot}42 \times 0{\cdot}38 \times 0{\cdot}48$ mm), aligned on Nicolet *R3m/E* diffractometer with Mo target, normal-focus tube, graphite monochromator and 0·5 mm pinhole collimator. Lattice parameters calculated from 25 reflections with $26 \le 2\theta \le 28°$. Systematic absences: $h + k = 2n + 1$ in entire reciprocal lattice; $l = 2n + 1$ for $h0l$ layer; $k = 2n + 1$ for $0k0$ axis. 2553 reflections measured at ~ 173 K (chilling under stream of N_2 with LT-1 device) over period of 30 h utilizing the $\theta/2\theta$ scan technique (variable scan speed from 6·0 to 29·3° min^{-1}; background/scan time = 0·1) within the ranges $3{\cdot}7 \le 2\theta \le 45°$, $0 \le h \le 15$, $0 \le k \le 19$, $-20 \le l \le 20$. Intensities of three standard reflections ($39\bar{4}$; $\bar{1},\bar{1},10$; $\bar{6}2\bar{6}$) recorded after every 100 reflections. 78 standard reflections decreasing linearly by < 1·0%, used to correct the remaining 2062 unique observed reflections [$F_o > 2{\cdot}5\sigma(F_o)$]. Data corrected for Lorentz and polarization effects. No absorption correction applied. All non-H atoms immediately located by direct-methods structure solution utilizing *SHELXTL* 4·0 (Sheldrick, 1983). All 26 H atoms located in subsequent difference Fourier synthesis. Structure refined by block cascade least squares with anisotropic thermal parameters for all atoms except H to minimize $\sum w(|F_o - F_c|^2)/\sum F_o^2$. H-atom thermal parameters taken as 1·2 times equivalent isotropic parameter of the bonded atom. H-atom position parameters fixed in calculated positions in the final stages of refinement. Final $R = 0{\cdot}045$ and $wR = 0{\cdot}052$ for 154 variables with $w = 1/[\sigma(F_o)^2 + 0{\cdot}0002(F_o)^2]$ and $S = 1{\cdot}29$. Maximum least-squares shift/e.s.d. = 0·016 in final refinement cycle. Maximum peak less than 0·3 e Å^{-3} in final Fourier map. Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974). All computer programs belong to the *SHELXTL* system.

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Discussion. Final positional and isotropic thermal parameters for the non-H atoms are given in Table 1 and the bond lengths and angles are given in Table 2.* The corresponding e.s.d.'s for the least-significant digits are shown in parentheses. A computer-generated plot in Fig. 1 shows the molecular structure. Numbered atoms represent the crystallographic asymmetric unit.

A short interatomic distance exists between the K and N atoms of the amide base and the same atoms of a symmetrically equivalent molecule generated by inversion through a center. Hence the aggregation state of potassium hexamethyldisilazide in the crystal is dimeric. No other unusual short intermolecular contacts were noted. A view of the packing is given in Fig. 2.

Table 1. *Atom coordinates* ($\times 10^4$) *and thermal parameters* (Å^2 $\times$ 10^3)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
K	1089 (1)	2701 (1)	4930 (1)	28 (1)
Si(1)	2233 (1)	1008 (1)	6081 (1)	27 (1)
Si(2)	2105 (1)	903 (1)	4127 (1)	25 (1)
N	2194 (2)	1338 (2)	5083 (2)	25 (1)
C(1)	3567 (3)	981 (2)	6641 (2)	42 (1)
C(2)	1476 (4)	1660 (2)	6756 (2)	50 (2)
C(3)	1730 (3)	−8 (2)	6237 (2)	38 (1)
C(4)	3385 (3)	786 (2)	3697 (2)	34 (1)
C(5)	1517 (3)	−103 (2)	4044 (2)	37 (1)
C(6)	1326 (3)	1514 (2)	3303 (2)	42 (1)
C(7)	1128 (3)	6890 (2)	4347 (2)	30 (1)
C(8)	1091 (3)	6311 (2)	4962 (2)	30 (1)
C(9)	1125 (3)	6492 (2)	5823 (2)	38 (1)
C(10)	1180 (3)	7261 (3)	6077 (3)	46 (1)
C(11)	1215 (3)	7846 (2)	5476 (3)	47 (2)
C(12)	1192 (3)	7659 (2)	4623 (3)	39 (1)
C(13)	1120 (3)	6682 (3)	3424 (2)	47 (2)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

K–N	2·745 (3)	K–K*a*	3·775 (1)
K–N*a*	2·801 (3)	Si(1)–N	1·671 (3)
Si(1)–C(1)	1·894 (4)	Si(1)–C(2)	1·894 (4)
Si(1)–C(3)	1·882 (4)	Si(2)–N	1·677 (3)
Si(2)–C(4)	1·895 (4)	Si(2)–C(5)	1·884 (4)
Si(2)–C(6)	1·892 (4)	N–K*a*	2·801 (3)
C(7)–C(8)	1·391 (5)	C(7)–C(12)	1·383 (5)
C(7)–C(13)	1·500 (5)	C(8)–C(9)	1·391 (5)
C(9)–C(10)	1·372 (6)	C(10)–C(11)	1·381 (6)
C(11)–C(12)	1·383 (6)		

N–K–K*a*	47·7 (1)	N–K–N*a*	94·2 (1)
K*a*–K–N*a*	46·5 (1)	N–Si(1)–C(1)	112·9 (2)
N–Si(1)–C(2)	111·3 (2)	C(1)–Si(1)–C(2)	105·7 (2)
N–Si(1)–C(3)	117·2 (2)	C(1)–Si(1)–C(3)	103·9 (2)
C(2)–Si(1)–C(3)	104·8 (2)	N–Si(2)–C(4)	112·6 (1)
N–Si(2)–C(5)	117·3 (2)	C(4)–Si(2)–C(5)	104·8 (2)
N–Si(2)–C(6)	111·1 (2)	C(4)–Si(2)–C(6)	104·8 (2)
C(5)–Si(2)–C(6)	105·2 (2)	K–N–Si(1)	109·6 (1)
K–N–Si(2)	107·9 (1)	Si(1)–N–Si(2)	133·8 (2)
K–N–K*a*	85·8 (1)	Si(1)–N–K*a*	104·8 (1)
Si(2)–N–K*a*	103·7 (1)	C(8)–C(7)–C(12)	117·4 (3)
C(8)–C(7)–C(13)	120·9 (3)	C(12)–C(7)–C(13)	121·7 (3)
C(7)–C(8)–C(9)	121·7 (3)	C(8)–C(9)–C(10)	119·6 (4)
C(9)–C(10)–C(11)	119·7 (4)	C(10)–C(11)–C(12)	120·2 (4)
C(7)–C(12)–C(11)	121·4 (4)		

The dimeric structure reported herein can be compared with the dioxane-solvated monomer reported by Domingos & Sheldrick (1974). The major differences between these two structures are the aggregation state (dimeric and monomeric respectively) and the co ordination number of the K atom (2 and 5 respectively). Bond lengths and bond angles are nearly identical in the two structures indicating similar *pπ–dπ* bonding between Si and N atoms. A number of Li- and Na-containing bis(trimethylsilyl)amide crystal structures are also known and can be compared with the potassium bis(trimethylsilyl)amide structures; references are as follows: Mootz, Zinnius & Bottcher (1969); Gruning & Atwood (1977); Rogers, Atwood & Gruning (1978); Lappert, Slade, Singh, Atwood, Rogers & Shakir (1983); Engelhardt, May, Raston & White (1983); Power & Xiaojie (1984); Tilley, Andersen & Zalkin (1984); Murray & Power (1984*a*,*b*); Becker, Hartmann, Munch & Riffel (1985).

Determination of the solution-phase aggregation state of the potassium dimer as well as a comparison of the reactivity of a number of alkali-metal amide bases towards ketones and esters is in progress.

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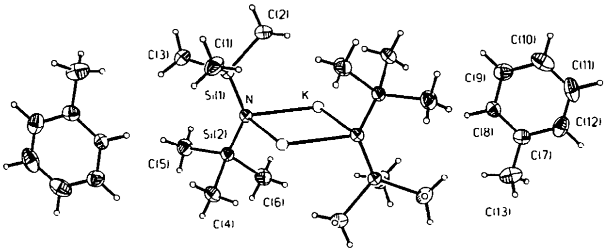

Fig. 1. Dimeric potassium hexamethyldisilazide.

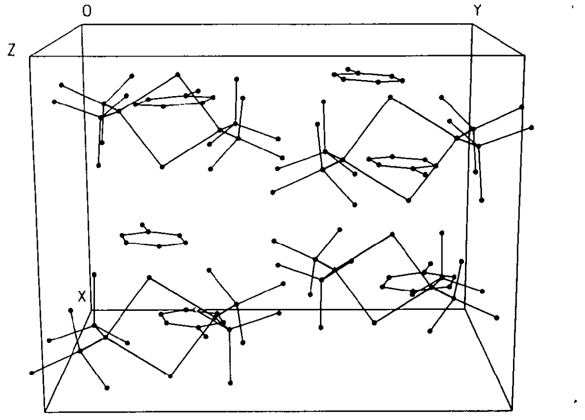

Fig. 2. Packing diagram.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44320 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 1,1′-Methylenebis(4,4′-dimethylaminopyridinium) Iodide

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Abstract. $C_{15}H_{22}N_4I_2.H_2O$, $M_r = 530{\cdot}2$, monoclinic, $C2/c$, $a = 19{\cdot}064\ (5)$, $b = 9{\cdot}085\ (3)$, $c = 11{\cdot}471\ (4)$ Å, $\beta = 92{\cdot}81\ (2)°$, $V = 1984\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}77\ \text{g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 31{\cdot}4\ \text{cm}^{-1}$, $F(000) = 1024$, $T = 293$ K, $R = 0{\cdot}040$, $wR = 0{\cdot}044$ for 3088 observed reflections. In spite of the anomalous NMR chemical shift of the methylene protons flanked by two positively charged N atoms and the absence of the characteristic downfield displacement of the NMR signal of the α protons due to quaternization of the ring N, X-ray crystallography results confirm that quaternization unequivocally takes place at the ring N.

Introduction. Since its introduction, high-resolution nuclear magnetic resonance (NMR) has become accepted as one of the most versatile analytical tools available to organic chemists. The NMR chemical shifts depend on the nature and position of the substituent and the molecular environment. As opposed to the benzene ring, the presence of the heteroatom in the pyridine ring causes subtle changes in the chemical environment of the aromatic protons. Thus the unshared pair of electrons of the ring N leads to differential shifts of the α, β and γ protons and thus three distinct signals for three types of protons are observed. The β protons are displaced upfield, the α protons appear farthest downfield and the γ protons somewhere in the middle (Spiesecke & Schneider, 1961). The presence of an exocyclic N introduces additional complications. NMR has been used to study the relative reactivity of the ring and the exocyclic nitrogens towards protonation and alkylation reactions (Essery & Schofield, 1961). Well defined changes occur in the NMR spectrum of the pyridines on quaternization. The presence of a positive charge on the N leads to lower screening for the neighboring protons. Consequently, the α protons can easily be distinguished by downfield displacement of their NMR signal. This characteristic feature is usually employed as a positive indication of the quaternization of the pyridine N (Smith & Schneider, 1961; Silverstein & Bassler, 1967; Sudmeier & Reilly, 1964).

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