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Lithium dicyanamide, its reactions with cyanuric chloride, and the crystal structures of $LiN(CN)_2(MeCN)_2$ and $LiCN(C_5H_5N)_2$

Andrew P. Purdy,* Eric Houser and Clifford F. George

Naval Research Laboratory, Chemistry Division Code 6120 and Laboratory for the Structure of Matter, Code 6030, Washington DC 20375, U.S.A.

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Abstract—Reactions of dicyanamides with cyanuric chloride were investigated as possible routes to carbon nitrides. Anhydrous lithium dicyanamide (**1**) was synthesized from $NaN(CN)_2$ and LiCl in THF. Compound **1** was found to react with cyanuric chloride to form a yellow product, which forms an amorphous lithium–carbon nitride with an approximate formula $CN_{0.7}Li_{0.2}$ upon thermolysis to 700°C. Upon heating to 1000°C, the product decomposes with the distillation of lithium cyanide. Reactions between cyanuric chloride and trimethylstannyl dicyanamide were also investigated. Lithium dicyanamide was also found to trimerize and polymerize at 280–320°C. Additionally, two Li–C–N complexes were structurally characterized. The bis (acetonitrile) adduct of **1** crystallizes with the lithium atoms linking the cyano nitrogens into infinite Li—N≡C—N—C≡N— chains, and the bis(pyridine) adduct of LiCN consists of infinite zig-zag —Li—C≡N— chains. © 1997 Elsevier Science Ltd

Keywords: lithium dicyanamide; lithium carbon nitride; carbon nitride; tricyanomelamine; lithium cyanide.

Interest in carbon nitride chemistry has increased in the last decade, mostly as a result of efforts to prepare superhard materials. Since carbon can form single, double, and triple bonds with both itself and nitrogen, an almost unlimited number of carbon nitride compounds and phases can exist [1]. There has been many recent reports of efforts (some successful) to prepare sp^3 bonded phases [1–3]. Well defined sp^2 bonded compounds, such as the polycyanogens [4], are known, as is an isomer of C_3N_4 postulated to consist of 2-dimensional, flat sheets [5]. Carbon nitrides of less well defined composition were prepared from the decomposition of $Hg(SCN)_2$ [6–8], and pyrolysis of various organics has been used to prepare C–N materials [9]. Molecular carbon nitrides such as $C_{15}N_{12}$ and $C_{18}N_{12}$ are also known [10]. As part of a study into the synthesis of nitride materials, we attempted to prepare carbon nitrides by chemical means. The simplest possible isomer of C_3N_4 is tri (cyano)amine, $N(CN)_3$, which has not been prepared in stable form [11]. If one could replace the chlorines in cyanuric chloride [$(CNCl)_3$] with dicyanamide [$N(CN)_2^-$] groups, the result would be a trimer of tri(cyano)amine, which could polymerize further to an extended C–N solid.

EXPERIMENTAL

General comments

All chemical manipulations were performed in a Vacuum-Atmospheres Dri-Lab or on a vacuum line. The sodium dicyanamide, cyanuric chloride, tetrahydrofuran, acetonitrile and trimethylstannylchloride were obtained from Aldrich Chemical Corp and used as received unless otherwise noted. The THF and acetonitrile were distilled from sodium benzophenone ketyl and P_2O_5, respectively, before use. The cyanuric chloride was sublimed under dynamic vacuum and recrystallized from CCl_4. Sodium dicyanamide was dried under vacuum at 250°C. The density of **4d** was measured by flotation in a $CH_2Cl_2/CHBr_3$ mixture. All infrared spectra of solids were recorded on KBr pellets using a Nicolet Magna-IR 750, and samples

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* Author to whom correspondence should be addressed.

were exposed briefly to the air before measurement. All NMR spectra were recorded on a Bruker AC-300 spectrometer. For ^{13}C spectra in D_2O solution, a small amount of ethanol (methyl = 17.2 ppm) was added as a reference. X-ray powder patterns were recorded on a Phillips diffractometer with a graphite crystal monochromator and $\lambda = 1.54050$ Å. TGA/DTA and DSC experiments were performed on TA Instruments SDT 2960 and DuPont 910 instruments respectively, at a heating rate of 10°C/min under an N_2 atmosphere. Elemental analyses were done by E+R Microanalytical Laboratories, Corona NY.

Synthesis of $LiN(CN)_2$ (**1**).

A mixture of $NaN(CN)_2$ (3.36 g, 37.7 mmol) and LiCl (1.50 g, 35.4 mmol) were stirred in 20 mL THF at 90–100°C (oil bath) for 2 days in an H-tube. After filtration and washing of precipitate, the THF was removed from the filtrate, and the residue dried at 100–110°C under vacuum for 1 day, affording the white solid $LiN(CN)_2$ (2.27 g, 88%). The product was further purified by recrystallization from acetonitrile and drying at 150°C under vacuum. Anal. Found (Calcd) for LiC_2N_3: C, 32.99 (32.92); H, 0 (0); N, 57.72 (57.58). IR: 3577(w), 3557(vw) (ν C$\equiv$N+ν_{as} C—N); 3247(vw) ($2\nu_s$ C—N+ν_{as} C—N); 3182(vw), 3092(w) (ν C$\equiv$N+ν_s C—N); 2744(vw); 2302(s) (ν_s C—N+ν_{as} C—N); 2245(s) (ν_{as} C$\equiv$N), 2173(vs) (ν_s C$\equiv$N), 1343(s), 1320(m) (ν_{as} C—N); 944(m) (ν_s C—N); 669(m) (δ C—N—C); 548(s) (δ N—C$\equiv$N); 511(s) (γ N—C$\equiv$N); assignments based on $NaN(CN)_2$. [12] NMR: ^{13}C; (THF) δ 118.5, (D_2O) 120.8.

Synthesis of $Li_3[C_3N_3(NCN)_3]$

The trimer was synthesized by heating $LiN(CN)_2$ powder (0.50 g) in a tube under 1 atm. of N_2 from room temperature to 380°C, and allowing it to stand at that temperature for 1 h. NMR: ^{13}C; (D_2O) 173.7 (triazine), 125.2 (C$\equiv$N).

Reaction of $(CNCl)_3$ *with dicyanamides*

(a) A mixture of $NaN(CN)_2$ (1.00 g, 11.2 mmol) and $(CNCl)_3$ (0.60 g, 3.25 mmol) were stirred in THF (10 mL) at 80–95°C for 5 days, and filtered twice. The remaining yellow solid shows only NaCl in its powder pattern (product is amorphous). A portion was heated under vacuum at 415°C for 1 h, washed with water, pumped dry under vacuum, and heated to 610°C under N_2, which resulted in a black solid. Anal. Found: C, 63.50; H, 0.97; N, 34.62. The yellow solid decomposed completely when heated to 700°C under vacuum. The infrared spectrum of the volatile materials showed the presence of $(CN)_2$, HCN, and a tiny amount of HCl. Cyanogen oligomers (or their protonated derivatives) were also present as determined by the mass spectrum: *m/e* 156 ($(CN)_6$, 1%), 116 (C_5N_4, 2%), 104 ($(CN)_4$, 100%), 90 (C_4N_3, 5%), 78 ($(CN)_3$, 10%), C_3N_2(5%), 52 ($(CN)_2$, 100%); for all of the latter, a protonated peak also was present. IR of unidentified species (gas phase): 2257(vs), 2281(vs), 3545, 3519, 3508, 3561.

(b) A mixture of $LiN(CN)_2$ (0.201 g, 2.75 mmol) and $(CNCl)_3$ (0.168 g, 0.91 mmol) were stirred in 15 mL THF for 1 day at 65°C and another day at 95–100°C. A yellow, insoluble, solid film formed on the walls of the flask. The mixture was filtered hot and washed twice. After grinding up the product, it was washed with THF several times more, and dried under vacuum at 100°C to remove most of the THF. Isolated yield: 0.211 g of **2a**. An attempt was made to remove LiCl with a soxhlet extractor using finely ground product and THF, but the analysis of the final product was almost identical.

A mixture of 4 equivs of $LiN(CN)_2$ (0.135 g, 1.8 mmol) and $(CNCl)_3$ (0.085 g, 0.46 mmol) was stirred for 3 days at 110°C in 15 mL THF affording **2b** after drying the product at 160°C in vacuo.

A mixture of $LiN(CN)_2$ (0.26 g, 3.6 mmol) and $(CNCl)_3$ (0.20 g, 1.1 mmol) was stirred in MeCN (15 mL) for 1 day at 130°C. The mixture was filtered, and the solids were washed with recondensed solvent followed by washing with THF 10 times (to remove LiCl). The solids were dried in vacuo at 150°C affording **2c** (341 mg).

A mixture of $LiN(CN)_2$ (2.50 g, 34.3 mmol) and $(CNCl)_3$ (2.00 g, 10.8 mmol) was stirred for 4 days at 100°C in 60 mL THF, filtered, and the solids washed 6 times with recondensed solvent. The yellow solid was dried in vacuo at 190°C affording **2d** (3.43 g).

(c) A mixture of $Me_3SnN(CN)_2$ (2.00 g, 8.7 mmol) and $(CNCl)_3$ (0.53 g, 2.9 mmol) was stirred in THF (30 mL) in an H-tube for 4 days at 110–115°C. After filtration, the solid was washed twice with recondensed solvent and dried in vacuo to 165°C. Isolated yield of 3: 1.11 g.

Hydrolysis of 2d

A 0.1 g portion of **2d** was stirred with an excess of H_2O. The volatile materials were dried over $MgSO_4$, then IR and NMR spectra were obtained.

Thermolysis of above products

All condensible gases were collected in cold traps at −196°C. (a) A 2.00 g sample of **2d** was pressed into a crumbly pellet in a die at 40,000 psi (to prevent splattering during thermolysis). The pellet was heated under dynamic vacuum at 400°C for 1h, and at 720–735°C for 14 h. A small amount of unidentified white sublimate was formed during heating. The black product was washed with NH_3 (1) at room temperature using a thick-walled H-tube (to remove any salts), and reheated at 700–740°C for 6 h in vacuo affording 353 mg **4d**. Anal. Found: C, 50.5; H, <0.1; N, 41.7; Li, 5.5; Cl, <0.5. XRD: broad amorphous peaks at d 4.7 and 3.4.

A 100 mg sample of **4d** was loaded into a quartz tube under quartz wool (to prevent splattering) and slowly heated in a furnace horizontally to 1100°C over 3 h. After cooling, a white solid (27.5 mg) was scraped from the top of the tube. Recrystallization of the solid (mp: 160°C, IR: 2109(vs) C≡N str), 453(s)) from pyridine afforded LiCN·Py_2 (**6**). Data for **6**: NMR: ^{13}C (C_5D_5N, 350 K) δ 166.8; mp: 111–115°C.

(b) A 34.4 mg sample of **2b** was slowly heated under dynamic vacuum to 700°C. The volatile materials to 400°C, 400–550°C, and 550–700°C were collected in traps and analyzed by IR. A small amount of an unidentified white sublimate appeared around 560°C. A black product **4b** (5.2 mg) was isolated; Anal. Found: C, 49.8; H, 0.0; N, 41.0.

(c) A 236 mg sample of **3** was heated in stages to 700°C under dynamic vacuum, and the evolved gases analyzed by NMR and IR. From 25–165°C, Me_3SnCl, Me_4Sn, THF, and other methyl tin species were observed, from 165–250°C mostly non-condensibles, from 250–490°C mostly methane, THF, HCN, Me_3SnCl, and other unidentified species, and from 500–700°C mostly HCN and $(CN)_2$ were present. A black residue (53 mg) (**5**) was isolated; Anal. Found: C, 21.0; H, 0.5; N, 11.1; Sn, 67.2; Cl, 0.

Crystal structure determinations

A suitable crystal of **1a** was mounted in a thin walled glass capillary with a small amount of MeCN to prevent solvent loss. The data were collected in the θ/2θ mode on an automated Siemens P4 diffractometer equipped with an incident beam graphite monochromator using Mo–Kα radiation. The data were corrected for Lorentz and polarization effects. The structure was determined by direct methods and refined using full matrix least-squares methods as implemented by the program SHELXL [13]. The coordinates and anisotropic thermal parameters were refined for all the non-hydrogen atoms. Hydrogen atoms were refined isotropically with fixed thermal parameters.

A small crystal of **6** was immersed in Cargille NHV oil and transferred into a −75°C nitrogen stream. The data were collected using Cu–Kα radiation from a Rigaku rotating anode equipped with X-ray mirrors and a Siemens SMART [14] CCD area detector system. The structure was determined by direct methods and refined using full matrix least-squares methods as implemented by the program SHELXL [13]. The coordinates and anisotropic thermal parameters were refined for all the non-hydrogen atoms. The asymmetric unit is the dimer $(LiCNPy_2)_2$ in which the C≡N group atoms are disordered with respect to atom order such that C and N atoms may occupy the same site. The absolute configuration cannot be determined from the data, and the choice of space group $P32_221$ is arbitrary. Hydrogen atoms were placed in idealized positions (C—H = 0.96 Å) and the coordinate shifts for carbon were applied to the bonded hydrogens. The isotropic thermal parameters for the hydrogens were fixed. Additional data collection and refinement parameters are given in Table 1.

RESULTS AND DISCUSSION

Reaction of cyanuric chloride with dicyanamides

Replacement of the three Cl atoms in cyanuric chloride with $N(CN)_2$ groups should result in $(CN)_3(N(CN)_2)_3$, an isomer of C_3N_4 (Eq. 1). Cyanuric chloride reacted with the commercially available $NaN(CN)_2$ in dry THF at elevated temperature to form an insoluble amorphous yellow product and NaCl. However, it was not possible to remove the salt without using protic solvents, which reacted with the yellow product. In order to do this metathesis, both $M(N(CN)_2)$ and MCl needed to be soluble in organic solvents.

$$(CNCl)_3 + 3MN(CN)_2 \rightarrow (CN)_3[N(CN)_2]_3 + 3MCl \qquad (1)$$

As the system with M = Li seemed to be a likely candidate, we prepared $LiN(CN)_2$ (**1**) from a metathesis reaction between $NaN(CN)_2$ and LiCl in dry THF, and purified the $LiN(CN)_2$ by recrystallization from acetonitrile. In contrast to the sparingly soluble $NaN(CN)_2$, **1** proved to be extremely soluble in THF and MeOH (but not Et_2O) and should be useful whenever an organic soluble source of the dicyanamide ion is required.

Reactions of **1** with $(CNCl)_3$ in THF (or MeCN) at 100–110°C form a bright yellow (**2a, 2b, 2d**) or orange (**2c**) air-sensitive solid. Most, but not all, of the lithium was washed out of the product with THF as LiCl (identity of latter was verified by powder diffraction). Table 2 lists the elemental analyses of the products after washing and vacuum drying at elevated temperature. A substantial discrepancy exists between those analyses and the ideal elemental composition of C_3N_4 (Table 2, Column A). This discrepancy has several possible causes; the presence of hydrogen must come from retention of (and possible reaction with) solvent, chlorine could come from either retention of LiCl or incomplete replacement of Cl on $(CNCl)_3$, and lithium could come from either retention of LiCl or $LiN(CN)_2$. The amount of chlorine in the product is less than can be accounted for by simple retention of lithium chloride and solvent (Column B), although retention of solvent and both LiCl and $LiN(CN)_2$ can account for the observed analyses (Column C). Incomplete replacement of the chlorines on the triazine, combined with retention of one equiv. of lithium

Table 1. Crystal and refinement data

	1a	**6**
Empirical formula	$(LiN(CN)_2 \cdot 2MeCN)_n$	$(LiCN \cdot Py_2)n$
Crystal system	orthorhombic	trigonal
Space group	Pmmn	$P3_221$
a (Å)	7.610(2)	9.149(2)
b (Å)	10.877(2)	9.149(2)
c (Å)	5.622(1)	47.974(10)
α (°)	90	90
β (°)	90	90
γ (°)	90	120
V (A^3)	465.4(2)	3477.4(11)
Z	2	6
Formula weight	155.1	382.32
F(000)	160	1200
ρ(calc), g cm^{-3}	1.107	1.095
Temp (°C)	22	−75
Crystal dim. (mm)	0.32 × 0.38 × 0.42	0.02 × 0.25 × 0.30
λ (Å)	0.71073	1.54178
μ (mm^{-1})	0.074	0.525
2θ max., (°).	50	118
Data collected, $h\ k\ l$	0 to 9, 0 to 12, 0 to 6	−9 to 9, −7 to 10, −40 to 48
Reflections collected	489	11126
Unique data	468	2949
R_{int}	0.007	0.084
Unique data, $I_o > 2\sigma(I_o)$	218	1868
Parameters refined	47	273
[a]R, [b]wR^2, S	0.048, 0.110, 1.02	0.071, 0.148, 1.03
Fourier excursions eA^{-3}	0.11, −0.14	0.17, −0.18

[a] $R = \Sigma|\Delta|/\Sigma|F_o|$; $\Delta = |F_o| - |F_c|$

[b] $wR^2 = [\Sigma[(w\Delta^2)^2/\Sigma[(wF_o^2)^2]]^{1/2}$; $\Delta = F_o^2 - F_o^2$

Table 2. Elemental analysis of reaction products from $(CNCl)_3$ + dicyanamides

#	Products (Found)				Theory (Calcd)			
	2a[a]	**2b**[a]	**2c**[a]	**3**[a]	(**A**)[b] (C_3N_4)	(**B**)[b]	(**C**)[b]	(**D**)[b]
C	41.0	39.9	38.9	33.1	39.1	39.6	40.3	40.1
H	1.6	1.7	0.9	2.2	0	1.1	1.3	1.3
N	52.1	51.6	53.0	37.6	60.9	51.3	51.9	51.5
Li	1.1	1.9	1.2	—	0	1.0	1.8	1.8
Cl	3.6	2.5	2.4	5.7	0	4.9	2.3	2.8
Sn	—	—	—	18.2	—	—	—	—

[a] **2a**—$3LiN(CN)_2 + (CNCl)_3$ in THF; **2b**—$4LiN(CN)_2 + (CNCl)_3$ in THF; **2c**—$3LiN(CN)_2 + (CNCl)_3$ in MeCN; **2d**—a large scale repeat of **2a**; **3**—$3Me_3SnN(CN)_2 + (CNCl)_3$ in THF.

[b] Column **A**—C_3N_4; Column **B**—$(C_9N_{12}[LiCl(THF)]_{0.45})$; Column **C**—$(C_9N_{12})(LiCl)_{0.25}(LiC_2N_3)_{0.75}(THF)_{0.6}$ Column **D**—$(CN)_3Cl_{0.3}(C_2N_3)_{2.7}LiN(CN)_2(THF)_{0.6}$ The proportions of retained LiCl, LiC_2N_3, and THF in Cols **B** and **C** and the extent of reaction and retained THF in col **D** were adjusted until a best fit to the experimental analyses was obtained.

dicyanamide per triazine unit also produced a good match to the observed analyses (Column D), particularly when 4 equiv. of **1** was used in the reaction. Hydrolysis of **2d** released THF, but produced no detectable HCl. The latter may indicate the most of the C—Cl bonds reacted with **1**, but the data are insufficient to draw more definite conclusions.

An infrared spectrum of the yellow solid **2d** clearly shows the presence of C—N single, double and triple bonds, and C—H bonds and is depicted in Fig. 1. The reaction of **1** with 3 equiv. $(CNCl)_3$ also proceeds slowly at ambient temperature, and was studied by ^{13}C NMR. After 3 days, a saturated solution has turned deep yellow and there are numerous peaks in the triazine region 160–180 ppm and the cyanide region of 90–120 ppm. A sharp peak at δ 95.2 is probably from ClCN [15], which may indicate degradation of the triazine ring. As the reaction proceeds, LiCl crystals form, and the solution becomes orange and substantially more viscous. Eventually phase separation of the polymeric products occurs. The large number of peaks over a broad range may indicate some rather complex reaction chemistry. Selected spectra are displayed in Figure 2.

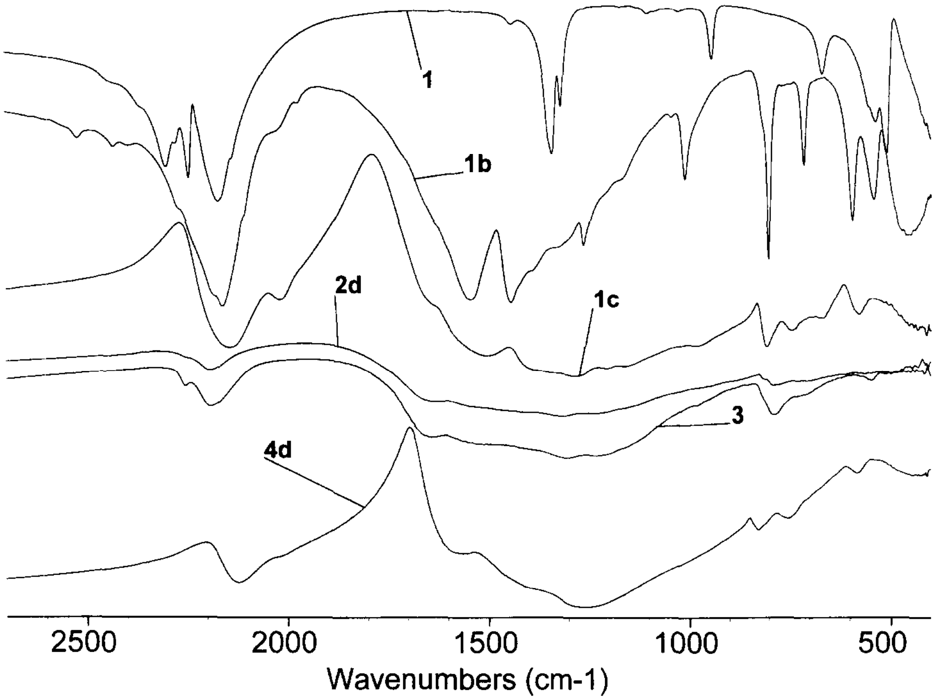

Fig. 1. Infrared transmission spectra (KBr pellet) of **1**–**4**.

Trimethylstannyl dicyanamide [16] is also soluble in THF. It does not react at ambient temperature with cyanuric chloride, but forms a yellow solid (**3**) at 110°C. The yellow solid (Table 2) incorporates a substantial amount of methyl tin species as evidenced by its analysis and decomposition behavior. Its infrared spectrum is very similar to **2d** with exactly the same $C\equiv N$ stretching frequency (Fig. 1). These reactions clearly do not produce a simple replacement of $N(CN)_2^-$ for Cl^- on the triazine ring. A likely explanation for this can be found in the nature of the dicyanamide ion. The dicyanamide ion has four possible resonance forms, of which the ones with the negative charge on the cyano nitrogens are the most significant [17]. While this allows highly stable ionic compounds to form with the metal ion coordinated to both of the end nitrogens, it disfavors the formation of covalent species which must either bond to the central nitrogen, or only to one end. The incorporation of substantial amounts of metal into the products implies that either the metal is complexed by the product or the dicyanamide groups on the metal polymerize with the $C\equiv N$ groups in the product.

Some of the yellow solids were thermolyzed under vacuum to determine if carbon nitride materials could be produced. All condensible gases emitted were collected in vacuum traps for analysis by IR, MS, and in some cases NMR. To 400°C, only THF and cyanogen oligomer(s) were emitted from **2a**–**d**. Between 400 and 500°C, HCl and HCN were observed, NH_3 and HCN were emitted between 500 and 550°C, and from 550 to 700°C $(CN)_2$, HCN, and non-condensibles were obtained. The jet black solid residue from thermolysis to 700°C has only about 15% of the original mass and elemental analysis shows the empirical composition of **4d** (from pyrolysis of **2d**) to be $CN_{0.7}Li_{0.2}X$, where C, N, and Li account for 98% of mass. The composition of **4b** is similar. Material **4d** had a density of 1.74 g/cm^3. The material from the pyrolysis of **3** to 700°C (**5**) has a composition approximating $CN_{0.5}H_{0.3}Sn_{0.3}$, and its X-ray powder pattern showed the presence of tin metal [18] as the only crystalline phase. Infrared spectra of **4d** show the complete loss of C—H bonds, a shift in the $C\equiv N$ stretch to 2120 cm^{-1}, and a loss of the peak at 790 cm^{-1}. Additional thermolysis of **4d** to above 1000°C resulted in the distillation of a colorless compound which was identified as lithium cyanide by its melting point [19] and the crystal structure of its pyridine adduct $(LiCN \cdot Py_2)_n$ (**6**). Some reaction with the quartz vessel occurred during the high temperature thermolysis. Reaction with quartz is often observed with reactive lithium compounds at high temperatures; **1** also reacted with quartz when molten above 720°C, during which substantial amounts of CO_2, $(CN)_2$, and a small amount of HCN were evolved.

Thermolysis of $LiN(CN)_2$ (**1**)

When heated to approximately 300°C, **1** was transformed to a mixture of products, whose composition was highly dependent on the thermolysis conditions. When the conditions allowed for efficient heat transfer away from the polymerizing material, most of the product was soluble in water, and the soluble portion

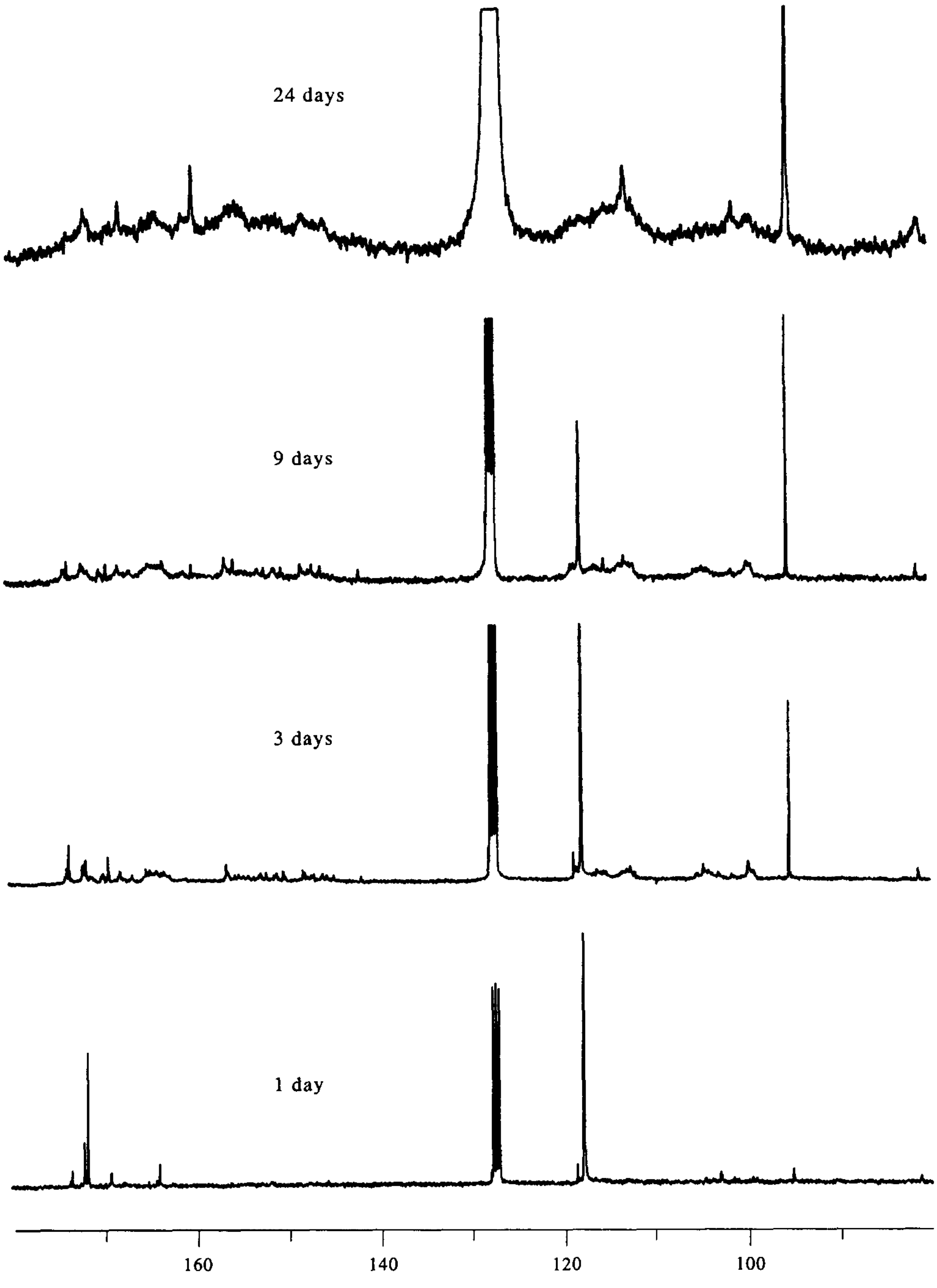

Fig. 2. Progress of a reaction between $(CNCl)_3$ and 3 equiv. of $LiN(CN)_2$ as monitored by ^{13}C NMR. Reaction was performed in THF with a few drops of C_6D_6 added for ^2D lock.

consisted entirely of a single compound (**1b**) as determined by ^{13}C NMR. The product **1b** had 2 peaks of equal integral in the ^{13}C NMR spectrum, which was consistent with trimerization to the Li salt of tricyanomelamine [Li_3(tcmel)]. This was confirmed by comparison to the ^{13}C NMR spectrum of the known compound Na_3(tcmel), which was identical [20]. Compound **1b** was soluble in H_2O, MeOH, and EtOH, but not in THF, pyridine, or NMP (1-methyl-2-pyrrolidinone). However, when **1** was thermolyzed in large quantity under dynamic vacuum, (especially as a pressed pellet from which heat cannot easily escape) a sudden, partial melting occurred around 310–320°C, and then the material rapidly solidified to a tan, largely insoluble, polymer (**1c**). Although the polymer had a bubbly, frothy appearance, no gas evolution was detected on the vacuum gauge during polymerization. The soluble portion of the latter contained **1b** and other unidentified products. Unlike **1**, sodium dicyanamide formed the trimer quantitatively under vacuum thermolysis, with no evidence of polymer formation. The reason for the different polymerization behavior of the Na and Li derivatives is not certain, but could be a steric effect due to the small size of the Li^+ ion. The infrared spectrum of **1b** had broad peaks at 1545 and 1445 cm^{-1} for the triazine stretching modes, but the polymer **1c** had a very broad group of absorptions from 1600 to 1000 cm^{-1}, similar to the products **2a–2d** and **3** Spectra of **1**, **1b**, and **1c** are reproduced in Fig. 1.

Thermal analysis experiments were performed to help understand the thermolysis of $LiN(CN)_2$ and $NaN(CN)_2$. A TGA/DTA experiment of **1** under N_2 showed a strong exotherm around 292°C corresponding to trimerization/polymerization (Fig. 3). Mass loss starts around 400°C (probably sublimation) and accelerates rapidly above 670°C (decomposition). There were endotherms near 575°C and 670°C. With $NaN(CN)_2$, the exotherm for trimerization occurred at a higher temperature (378°C), and mass loss did not occur until an endotherm at around 650°C (the mp of Na_3(tcmel))[21]. The final weight retained after thermolysis of **1** at 1000°C was 13%, and 1% for $NaN(CN)_2$. A DSC experiment on $NaN(CN)_2$ showed a single, strong exotherm at 379°C, which integrated to a heat of trimerization of 1.0 kcal/mole. The DSC of **1** showed an exotherm consisting of several overlapping peaks. The first peak was around 280°C, and the peak of the overall exotherm was 324°C. An integration of the peaks showed that almost the same amount of heat, 0.98 kcal, was evolved per mole of 1. This is not surprising, as one would expect the trimerization reaction to be much more exothermic than the condensation of the trimer into a polymer.

Crystal structures of $(LiN(CN)_2 \cdot 2MeCN)_n$ (**1a**) *and* $(LiCN \cdot 2Py)_n$ (**6**)

The structures of **1a** and **6** are depicted in Figs 4 and 5, respectively. Dicyanamide ions usually act as bridging ligands which are coordinated to metals through their cyano nitrogens [17], and **1a** is no exception. In **1a**, the $N(CN)_2^-$ groups link the Li^+ ions into a planar —Li—N≡C—N—C≡N— chain which is arranged parallel to the a axis. Two acetonitrile ligands coordinate each lithium, which makes Li 4-coordinate. The geometry around Li is approximately tetrahedral, with the angle between the two acetonitrile nitrogens (101.8(5)°) being significantly less and the other N—Li—N angles being slightly more than the tetrahedral angle at 109.5°. The C—N—C angle of almost 120° is typical for bridging dicy-

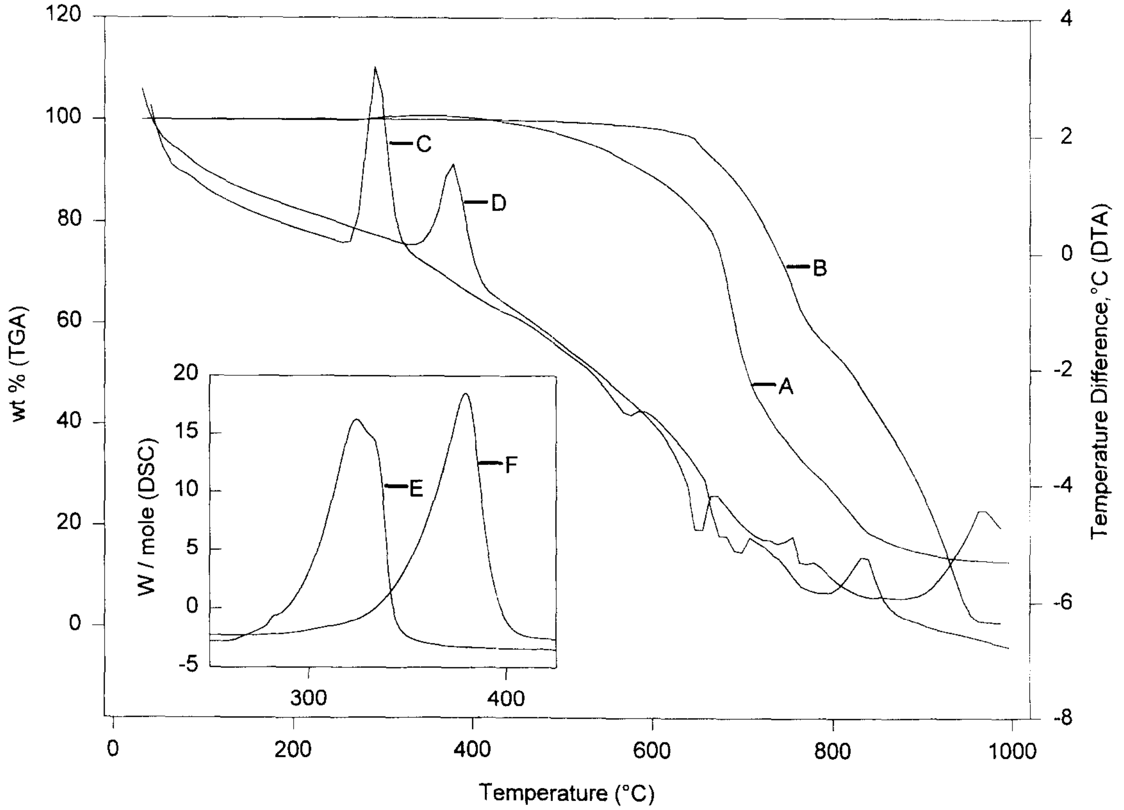

Fig. 3. Thermal analysis of $LiN(CN)_2$ (**1**) and $NaN(CN)_2$. Trace A = TGA of **1**, B = TGA of $NaN(CN)_2$, C = DTA of **1**, D = DTA of $NaN(CN)_2$, E = DSC of **1**, F = DSC of $NaN(CN)_2$.

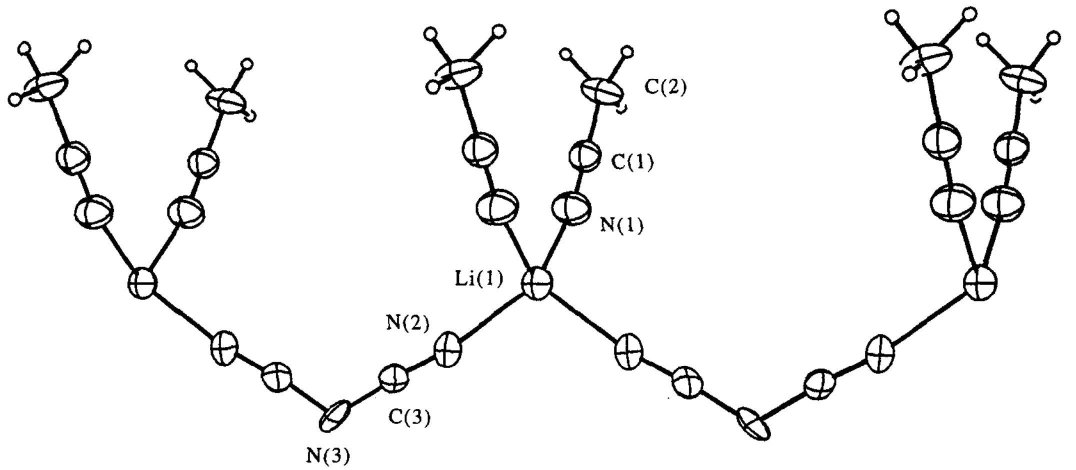

Fig. 4. Molecular structure of **1a**. Selected bond lengths (Å) and angles (°) : Li(1)–N(1) 2.051(7), Li(1)–N(2) 1.980(6), N(1)–C(1) 1.131(5), N(2)–C(3) 1.139(5), N(3)–C(3) 1.317(5), C(1)–C(2) 1.453(7), N(1)–Li(1)–N(2) 110.63(8), N(2)–Li(1)–N(2A) 112.0(5), Li(1)–N(1)–C(1) 164.2(4), Li(1)–N2–C(3) 171.6(4), C(3)–N(3)–C(3A) 119.2(5), N(1)–Li(1)–N(1A) 101.8(4), N(1)–C(1)–C(2) 179.3(5), N(2)–C(3)–N(3) 175.2(4).

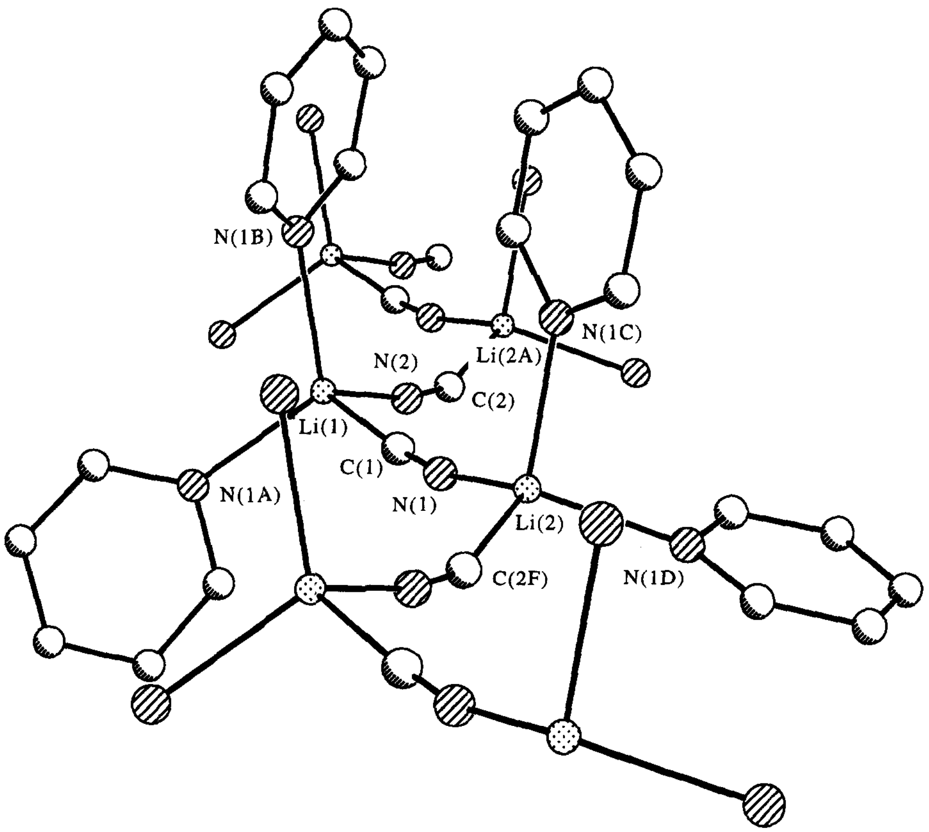

Fig. 5. Molecular structure of **6**; some pyridine carbons omitted for clarity. Selected bond lengths (Å) and angles (°) : Li(1)–C(1) 2.074(9), Li(1)–N(2) 2.046(10), Li(2)–C(2F) 2.049(10), Li(2)–N(1) 2.073(10), C(1)–N(1) 1.158(5), C(2)–N(2) 1.162(5), C(1)–Li(1)–N(2) 115.5(3), N(1)–C(1)–Li(1) 173.9(4), N(2)–C(2)–Li(2A) 162.2(4), C(2F)–Li(2)–N(1) 123.8(4), C(1)–N(1)–Li(2) 168.7(4), C(2)–N(2)–Li(1) 169.6(4).

anamide groups which have been observed from 116.7 to 130(1)° with a mean of 122° [22]. Both the C—N and C≡N bond distances in the N(CN)$_2^-$ ligand are comparable to other dicyanamide complexes, with the C≡N bond near the short end of the reported range 1.11(2)–1.19(5) Å while the C—N distance of 1.317(5) Å is near the long end of the observed range 1.237(15)–1.335 Å.

The structure of $(LiCN \cdot Py_2)_n$ (**6**) consists of infinite zig-zag —Li—N≡C— chains with bends of 115.5(3) and 123.8(4)° at Li(1) and Li(2), respectively. The disorder of the chain C and N atoms refined to equal occupancies. Thus, the labeling of the C and N atoms in Fig. 5 were chosen to make the structure self-consistent. The atoms Li(1), C(1), N(2), and their symmetry related equivalents within a chain consist of one plane which forms an angle of 44.7° to the plane formed by Li(2), N(1), C(2), and their equivalents. The chains lie in the ab plane and are related to each other by a 3_2 screw axis along c and by translation operations. Each Li atom is coordinated by 2 pyridine molecules in approximately tetrahedral configuration with the angles around Li ranging from 102.2(4) to 123.8(4)°.

Infinite M—C≡N—M chains are fairly common in cyanide complexes. When there are two different metals such as in $Et_4NLiHg(CN)_4$ [23] and $Me_4NLiFe(CN)_6 \cdot 2H_2O$ [24] the nitrogen of the CN^- ion usually coordinates to the more electropositive element. Cyanide networks with only one metal such as $Cd_4(CN)_9^-$ can coordinate both ends of the cyanide ion to prevent coordinative unsaturation [25]. In the parent compound LiCN, the Li ions are tetrahedrally coordinated to three nitrogen atoms and one carbon atom [19]. A similar coordination environment exists in **6** where pyridine molecules substitute for two Li–NC interactions of LiCN. The Li–NC distances are ordinary and comparable to those observed in the $Me_4NLiM(CN)_6 \cdot 2H_2O$ complexes [24], $Et_4NLiHg(CN)_4$ and to the shortest distances of LiCN. The C≡N—Li and N≡C—Li angles of 161.9(5)–174.0(4) are quite typical of cyanide linked chains, which normally deviate slightly from 180°.

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