J Chem Crystallogr (2011) 41:375–378
DOI 10.1007/s10870-010-9892-6

ORIGINAL PAPER

Crystal Structure of Dimerized 1,3-Diisopropyl Carbodiimide

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Received: 4 May 2010 / Accepted: 3 September 2010 / Published online: 17 September 2010
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Abstract A crystal structure of dimerized 1,3-diisopropyl carbodiimide (CDI) has been obtained and its synthesis through a reaction of CDI with aluminum chloride ($AlCl_3$) has been studied. It possesses space group $P2_1/c$, with $a = 9.352(5)$, $b = 7.956(4)$, $c = 11.405(6)$ Å and $\beta = 112.465(5)°$. It has been observed that this reaction is catalytic with respect to $AlCl_3$. Kinetic studies of the dimer show that its decomposition into CDI is first order with respect to the dimer. The reactivity of the dimer with metals has been investigated through reactions with methyl lithium and alane. The thermal stability of the dimer has been investigated by thermal gravimetric analysis and differential scanning calorimetry.

Keywords Carbodiimide · Crystal structure · Aluminum chloride

Introduction

Our interest in carbodiimides stem from their use in the synthesis of amidinates and guanidinates as ligands for metal centres; these compounds are then evaluated as potential vapour phase precursors for chemical vapour deposition (CVD) and atomic layer deposition (ALD) processes of aluminum oxide [1, 2]. We have also performed theoretical and synthetic investigations of carbodiimide insertion over aluminum compounds, proposing the mechanism illustrated in Scheme 1 [3]. Aluminum is often used as a starting point with new ligands due to its availability, ease of use and strong acidic nature. Compound **1** was first observed as a byproduct of our investigations; subsequent examination of its utility in the synthesis of volatile metal-bearing precursors showed little promise but an investigation of its synthesis and thermolysis was performed to extend our understanding of aluminum-carbodiimide interactions. Previous work on the synthesis of carbodiimide dimers is scarce but has been performed employing alkylating agents such as dimethyl sulphate in the absence of solvent at room temperature [4] and by a tandem aza-Wittig/[2 + 2] cycloaddition of carbodiimides employing bis(iminophosphoranes) [5, 6].

Experimental

A single crystal was mounted on a thin glass fiber using viscous oil and then cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in F. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.12 program library. CIF has been submitted under CCDC 775576.

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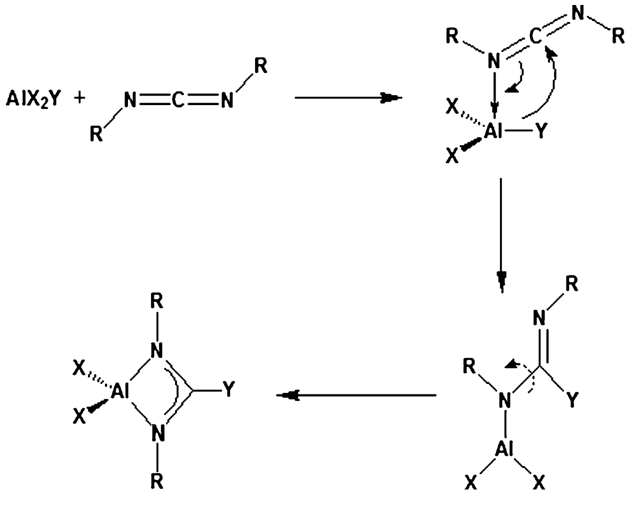

Scheme 1 Carbodiimide insertion mechanism [3]

General Procedures

All manipulations were performed in a glovebox under N_2 atmosphere. The 1,3-diisopropyl carbodiimide (CDI), aluminum chloride ($AlCl_3$), and all anhydrous grade solvents were purchased from Aldrich and used as received. The ^1H NMR spectra were recorded on a Bruker AMX 300 spectrometer at ambient probe temperature, using the residual protons in the deuterated solvent for reference. The deuterated benzene was purchased from Aldrich and used as received.

*Compound **1***

1,3-Diisopropyl carbodiimide (5.762 g, 45.7 mmol) was added to a solution of hexanes (15 mL), ether (5 mL) and $AlCl_3$ (2.030 g, 15.2 mmol) in a round bottom pressure vessel. The resulting clear yellow solution was stirred rapidly and refluxed for 3 days at 120 °C. The resulting upper yellow liquid phase was decanted and kept at −30 °C until crystals of **1** were formed and collected. Hexane was added to the vessel containing the lower red viscous liquid phase and stirred overnight for additional extraction (5.04 mm, 22.1%). ^1H NMR (300 MHz, C_6D_6): δ 3.76 (sept, 2H, C=NCH(Me)$_2$), 3.61 (sept, 2H, NCH(Me)$_2$), 1.30 (*d*, 12H, C=NCH(CH$_3$)$_2$), 1.20 (*d*, 12H, NCH(CH$_3$)$_2$).

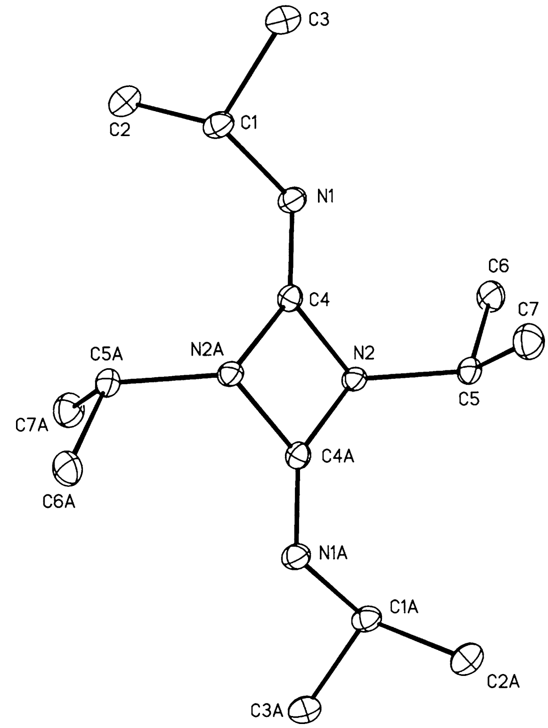

Fig. 1 Molecular diagram and atomic labelling scheme of **1**. Hydrogen atoms have been omitted for clarity, and the thermal ellipsoids are shown at 30% probability

Results and Discussion

A molecular diagram of **1** is given in Fig. 1. The strained heterocycle is the most interesting feature and it dominates the structure. The C–N distances in the heterocycle are essentially equivalent with an average length of 1.427 Å, which is comparable to similar structures [6–8]. The heterocycle is planar with a slightly smaller angle between the C–N–C bonds (88.25°) as compared to the N–C–N angles (91.75°). The exocyclic moieties show deviations from ideal geometries partly due to the strain of the heterocycle and partly due to steric repulsion induced on one another. The sum of angles around N2 (328.74°) show a mild deviation from ideal pyramidilization. The sum of angles around C4 (359.5°) similarly show a very slight deviation from the ideal planar structure. This is further highlighted by the torsion angle C1–N1–C4–N2A of 1.60°, clearly demonstrating that the N1–C4 double bond is not co-planar with the ring (Tables 1, 2, 3).

With respect to the synthesis of **1**, it was found that the reaction of CDI with $AlCl_3$ was catalytic with respect to $AlCl_3$ and would not proceed at temperatures below 120 °C. Similar catalytic and non-catalytic activity of aluminum species with carbodiimides has been shown previously [7, 9, 10]. Analysis of the red viscous product by ^1H NMR was inconclusive, but these data in addition to the viscosity of the liquid suggest that it may consist of higher order oligomers of CDI.

The dissociation kinetics of **1** were studied via a sealed thick-walled NMR tube thermolysis experiment. The tube was heated using an oil bath held at 150 °C for the duration of the rate study and removed for ^1H spectrum acquisition

Table 1 Crystal data summary

CCDC no.	775576
Empirical formula	$C_{16}H_{28}N_4$
Formula weight (g/mol)	252.4
Colour/shape	Colourless/plate
Temperature (K)	120(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	9.352(5)
b (Å)	7.956(4)
c (Å)	11.405(6)
β (°)	112.465(5)
Volume (Å^3)	784.2(7)
Z	2
Density (kg/L)	1.07
Absorption coefficient (mm^{-1})	0.07
Diffractometer	Bruker AXS APEX
Reflections collected	8282
θ range for data collection (°)	2.36–28.27
Limiting indices	$-12 \le h \le 11$, $-10 \le k \le 10$, $-15 \le l \le 14$
Independent reflections	1813
Reflections with $I > 2\sigma(I)$	1554
Number of parameters	82
Goodness-of-fit on F^2	1.049

Table 2 Nonhydrogen fractional atomic coordinates and equivalent isotropic thermal parameters

	x	y	z	U (eq)
C1	0.32853(13)	−0.17084(14)	0.67633(11)	0.0213(3)
C2	0.34692(15)	−0.19161(16)	0.81381(11)	0.0275(3)
C3	0.48546(14)	−0.17012(16)	0.66552(12)	0.0272(3)
C4	0.11062(13)	−0.00906(13)	0.55736(10)	0.0175(3)
C5	0.05934(13)	0.24890(14)	0.41433(10)	0.0203(3)
C6	0.18098(15)	0.36649(15)	0.50201(12)	0.0285(3)
C7	0.11329(16)	0.16162(17)	0.32009(12)	0.0302(3)
N1	0.25174(11)	−0.01045(11)	0.62593(9)	0.0207(2)
N2	0.01376(10)	0.12637(11)	0.49095(8)	0.0178(2)

Table 3 Selected geometrical parameters

Compound	(Å, deg)
N2–C4	1.4252(14)
N1–C4	1.2508(16)
N2–C5	1.4766(15)
N2–C4–N2A	91.75(9)
C4–N2–C4A	88.25(9)
C4–N2–C5	123.03(9)
C5–N2–C4A	125.46(9)
N1–C4–N2	130.05(10)
N1–C4–N2A	138.16(10)
C1–N1–C4–N2A	1.6(2)
C5–N2–C4–N1	45.59(17)

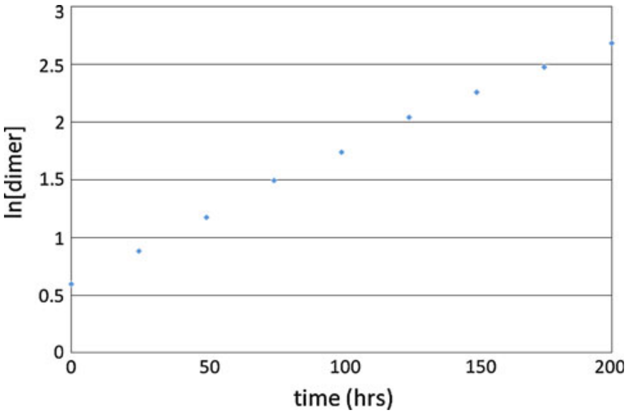

Fig. 2 Thermolytic dissociation of **1** at 150 °C

only. As the initial concentration of **1** dissociated into CDI, a comparison of the integration of their respective peaks at roughly 24-hour intervals was made, and checked against the integration of the native deuterated benzene and the peaks from adventitious ether. The peaks associated with both **1** and CDI that were used for this comparison were the isopropyl group doublets at 1.29 and 1.04 ppm, respectively. These peaks were chosen for their sharpness, intensity, and separation from other peaks. The ratio of the integration of the dimer peaks to the sum of the dimer and CDI peaks was plotted against time, resulting in a smooth curve showing **1** being depleted as the CDI was formed.

A linear relationship was found by taking the natural logarithm of the ratio as a function of time, showing that this is a straightforward first-order dissociation with respect to **1**, as shown in Fig. 2. The rate constant k is found from the slope of the ln[compound **1**] vs. time curve to be 3.036×10^{-6} s^{-1}. From this the half-life of dissociation can be calculated as 63.4 h.

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