Bull. Chem. Soc. Jpn., **74**, 699—700 (2001)

Conformation Preferences of 1,1′-Bis(1-amino-4,4-dicyclopropyl-2,3-diaza-1,3-butadienyl)

Yulin Lam,* Ngai Ling Ma,† and Eping Liang

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

†Institute of High Performance Computing, 89C Science Park Drive, #02-11/12, The Rutherford, Singapore 118261

(Received September 18, 2000)

The reaction of dicyclopropyl ketone with hydrazine sulfate and sodium cyanide afforded 1,1′-bis(1-amino-4,4-dicyclopropyl-2,3-diaza-1,3-butadienyl). The compound exists in the *trans* conformation in the solid-state and has a *trans* population of 91.2% in solution. Experimental data are compared with values estimated by ab initio calculations.

It is well established that the condensation of hydrazines with carbonyl compounds yields hydrazones, which in turn could undergo nucleophilic attack by a cyanide anion to provide the cyano-substituted hydrazine.[1] However, interestingly, we found that when dicyclopropyl ketone was treated with hydrazine sulfate and sodium cyanide, the compound isolated was not the expected cyano-substituted hydrazine but instead a conjugated amino compoud, which was identified as 1,1′-bis(1-amino-4,4-dicyclopropyl-2,3-diaza-1,3-butadienyl) **1**, was obtained. Herein we report our findings on **1** based on X-ray diffraction measurements, dipole moment determination, and ab initio calculations (Fig. 1, Tables 1, 2, and 3).

Molecule **1** exists in the *trans* conformation and has a remarkably short central C–C bond length of 1.492(2) Å. A plausible reason for this shortening of the C–C bond may be the modification of the s/p hybridization ratio by the electronic interaction of the diaza groups so as to increase the s character of the C–C bond.

Dipole moments of **1** are determined using the method of LeFevre and Vines.[2,3] The results show that the dipole moment values increase with increasing temperature. This implies the presence of more than one conformer in the solution and that the conformer with higher moment is of higher energy. Application of the Lennard–Jones–Pike[4] method of analysis yields a μ_g value equal to 23.48×10^{-30} Cm and an internal energy difference between the *gauche* and *trans* conformers, ΔE ($= E_g - E_t$) of 7.64 kJ mol^{-1}. The corresponding proportion of *gauche* conformer is 8.8% at 25 °C.

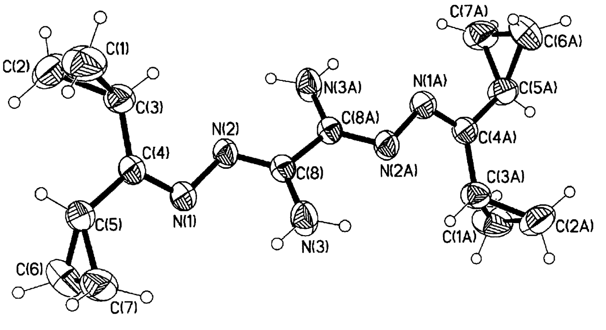

Fig. 1. Thermal ellipsoid diagram of **1**.

Molecular orbital calculations of **1** and its parent analogue 1,1′-bis(1-amino-2,3-diaza-1,3-butadienyl) **2** were performed so that the potential energy surface may be explored in detail. A series of constrained optimizations were performed at various levels of theories (AM1, PM3, HF/STO-3G, HF/3-21G, HF/6-31G(d), B3-LYP/6-31G(d)), where the torsion angle N(3)–C(8)–C(8A)–N(2A) is fixed at intervals of 10° from the range of 0° to 180°.

AM1 and PM3 potential energy surfaces of **2** show only one stable minimum (N(3)–C(8)–C(8A)–N(2A) of approximately 60°) whereas on the ab initio surfaces (HF/STO-3G, HF/3-21G, HF/6-31G(d), B3-LYP/6-31G(d)), two minima are found. The more stable conformer adopts a *trans* conformation with a central C–C bond of 1.497 Å, which is comparable to that obtained from the X-ray structure of **1**. This suggests that the C–C bond in this species of compounds is essentially a single bond and that relatively free rotation about this bond can be expected. Our best estimate at the B3-LYP/6-311+G(d,p)//B3-LYP /6-31G(d,p) level of theory suggested that ΔE ($E_g - E_t$) of **2** is 46 kJ mol^{-1}.

As with **2**, ab initio calculations of **1** show that the *trans* configuration is more stable than the *gauche*. The B3-LYP/6-31G(d) optimized structure of **1** is in good agreement with the crystal structure with the mean-absolute-deviation of bond lengths and angles being 0.017 Å and 0.6°, respectively. Whilst the theoretical structure is more planar (C(4)–N(1)–N(2)–C(8) being −172.3°), the mean-absolute-deviation of the remaining torsion angles is 3.6°.

Ab initio calculations show that the structural parameters of

Table 1. Crystal Data and Structure Refinement of **1**

Empirical formula	$C_{16}H_{24}N_6$
Formula Weight	300.41
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	5.2992(3)
b/Å	11.4756(6)
c/Å	13.6461(7)
β/°	97.1730(10)
U/Å^3	823.34(8)
Z	2
D_C/g cm^{-3}	1.212
μ/mm^{-1}	0.077
Crystal size/mm^3	$0.36\times0.12\times0.28$
θ range for data collection/°	2.33 to 29.39
Reflections collected	5117
Independent reflections	2011 [R (int) = 0.0144]
Final R indices [$I > 2$ sigma(I)]	$R1 = 0.0476$, $wR2 = 0.1450$
R indices (all data)	$R1 = 0.0543$, $wR2 = 0.1515$

Table 2. Bond Lenghts (Å), Bond Angles (°), and Torsion Angles (°) of **1** as Determined by X-ray Crystallography. Theoretical Geometrical Parameters are Included in Square Brackets: Normal-Style for the *trans* Form, and Italics-Style for the *gauche* Form

N(1)–C(4)	1.2868(16) [1.294, *1.296*]	N(1)–N(2)	1.4156(14) [1.392, *1.394*]
N(3)–C(8)	1.3481(16) [1.357, *1.384*]	C(1)–C(2)	1.469(3) [1.497, *1.497*]
C(1)–C(3)	1.504(2) [1.522, *1.522*]	C(3)–C(4)	1.4689(17) [1.486, *1.485*]
C(8)–C(8A)	1.492(2) [1.491, *1.488*]	C(4)–N(1)–N(2)	115.69(10) [116.6, *115.3*]
N(1)–C(4)–C(3)	124.57(11) [124.0, *123.7*]	N(1)–C(4)–C(5)	117.39(11) [116.7, *116.9*]
N(2)–C(8)–N(3)	125.23(10) [126.3, *125.0*]	N(2)–N(1)–C(4)–C(3)	−3.30(20) [1.8, *1.2*]
N(1)–N(2)–C(8)–N(3)	−1.99(18) [4.2, *6.9*]	C(4)–N(1)–N(2)–C(8)	139.57(13) [−172.3, *−174.2*]
C(2)–C(1)–C(3)–C(4)	−110.52(16) [−110.3, *−110.3*]		
N(3)–C(8)–C(8A)–N(3A)	180.00(11) [172.5, *17.5*]		
N(3)–C(8)–C(8A)–N(2A)	0.90(12) [−7.2, *−158.4*]		

Table 3. Molar Polarization, Refractions, and Dipole Moments at Infinite Dilution of **1**

T/°C	Solvent	Conc. range (10^5 w_2)	$\alpha\varepsilon_1$	β	γ	P_2/cm^3	R_D/cm^3	μ[a)]/10^{30} Cm
7	CCl_4	70–150	2.17	−0.798		164.7		6.21±0.02
25	CCl_4	80–180	3.70	−0.050	0.234	205.8	82.97	6.95±0.04
45	CCl_4	80–150	2.66	−0.749		184.9		7.44±0.02

a) $P_D = 1.05R_D$; R_D (calc) = 84.75.

1 and **2** are essentially identical, with a major difference occurring around C(4). Compared to **2**, the C(4)–N(1) bond in **1** is slightly longer by 0.016 Å, with a decrease in Wiberg bond order from 1.95 to 1.84. Calculation at the B3-LYP/6-311+G (d,p)//B3-LYP /6-31G(d,p) level of theory provides a ΔE of 34 kJ mol^{-1}. We note that the calculated ΔE of 34 kJ mol^{-1} is substantially larger than the experimental value of 7.6 kJ mol^{-1}. This difference might arise from the small basis set employed in the calculation and the neglect of solvent effect in the theoretical model. Nevertheless, our calculations are in good qualitative agreement for the system of interest.

Experimental

Preparation of 1. To a suspension of dicyclopropyl ketone (1.10 g, 10.0 mmol) in water were added sodium cyanide (0.59 g, 12.0 mmol) and hydrazine sulfate (0.80 g, 12.0 mmol), and the reaction mixture was shaken at room temperature for 8 days. The dark brown mixture formed was extracted with hot diethyl ether and the organic layer was decolorized with activated charcoal. Recrystallisation from diethyl ether gave colorless crystals of **1** (0.30 g, 20%), mp 188 °C. Anal. Calcd for $C_{16}H_{24}N_6$: C, 63.97; H, 8.05; N, 27.98%; MW, 300. Found: C, 64.21; H, 8.18; N, 27.60%; M$^+$, 300. ^{1}H NMR (500 MHz, $C_6D_5CD_3$; Me_4Si) δ 0.40 (s, NH_2), 0.42–0.46 (m, CH_2), 0.60–0.64 (m, CH), 0.64–0.69 (m, CH_2), 0.77–0.80 (m, CH_2), 0.91–0.94 (m, CH_2), and 2.87–2.93 (m, CH).

Dipole Moment Determination. Dielectric constants were determined with a heterodyne-beat meter,[5] and densities and refractive indices by standard procedures (Table 3).[3] The physical constants required in the dielectric measurements have been given previously.[6,7]

X-ray Crystallography. Crystals of **1** was obtained from diethyl ether. Data collection was performed at 298 K using a Siemens R3m/V200 diffractometer with Mo-$K\alpha$ radiation (λ = 0.71060 Å). Details of the crystal data and intensity collection are summarized in Table 1 and 2. The structure was solved by direct method and refined by full-matrix least-squares method using the SHELXTL-Plus PC program package.[8] Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were treated as riding on their attached atoms and were refined isotropically. List of final atomic coordinates, bond lengths and angles, thermal parameters and torsion angles have been deposited as Document No 74023 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited as Document No 155120 at the Cambridge Crystallographic Data Centre.

Calculations. Molecular orbital calculations were performed using Gaussian94 and Gaussian98 packages of program.[9] For stationary points obtained from full optimizations, the nature of these structures was confirmed using frequency analysis. All energetics reported are corrected with scaled (0.9) zero-point energies at the HF/6-31G (d) level.

References

1 F. E. Ziegler and P. A. Wender, *J. Am. Chem. Soc.*, **93**, 4318 (1971).

2 R. J. W. LeFevre and H. Vine, *J. Chem. Soc.*, **1937**, 1805.

3 R. J. W. LeFevre, "Dipole Moments, 3rd ed," Methuen, London (1953), Chap. 2.

4 J. E. Lennard-Jones and H. H. M. Pike, *Trans. Faraday Soc.*, **30**, 830 (1934).

5 H. H. Huang and E. P. A. Sullivan, *Aust. J. Chem.*, **3**, 1 (1965).

6 L. H. L. Chia, H. H. Huang, and P. K. K. Lim, *J. Chem. Soc. B*, **1969**, 608.

7 K. E. Calderbank, R. J. W. LeFevre, and G. L. D. Ritchie, *J. Chem. Soc. B*, **1968**, 503.

8 Siemens, "SHELXTL-PLUS, Release 4.20," Siemens Analytical X-ray Instruments Inc, Madison, Wisconsin, USA (1990).

9 "Gaussian 98, Revision A. 6," Gaussian, Inc., Pittsburgh PA (1998).