SATURATED POLYHETEROPERYLENES FROM THE REACTION OF GLYOXAL AND PYRUVALDEHYDE WITH 3-(2-HYDROXYETHYL)- and 3-(2-AMINOETHYL)-1,3-PROPANEDIAMINES AND PREDICTION OF THEIR STEREOCHEMISTRY[1]

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Abstract - Reaction of 3-(2-hydroxyethyl)- and 3-(2-aminoethyl)-1,3-propanediamines with glyoxal gave dioxatetraaza- and hexaazaperhydroperylenes. Each of the possible stereoisomers for the products was predicted by ^{1}H- and ^{13}C-nmr spectra and heats of formation from a molecular orbital method (AM1).

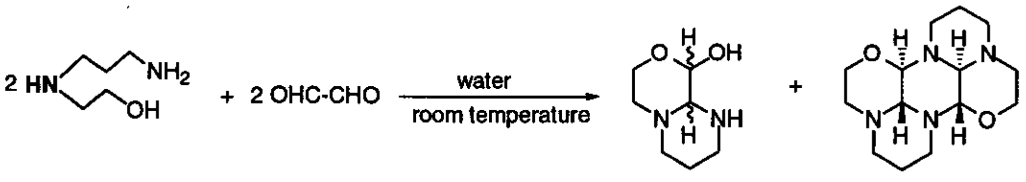
INTRODUCTION

Many polyfunctionalized compounds having amino and hydroxy groups react with mono- and di-carbonyls such as formaldehyde, glyoxal, 2,3-butanedione, benzil, and glutaraldehyde to give a variety of bicycles, tricycles, tetracycles, and caged compounds.[2-19] Consequently, it has been found that control by steric and lone pair - lone pair interactions predominate. Katritzky[20] predicted one of many possible isomers from the reaction of hydrazine with formaldehyde and hydrogen peroxide to be one-six- and two-seven-membered ring by heats of formation from a molecular orbital method (AM1). Similarly, we have predicted one of three expected stereoisomers of polyazaperylene from the reaction of hydrazinoethanol with formaldehyde using nmr spectra and AM1 and determined the structure by X-ray crystallography.[21]

In a continuation of our work on the reaction of polyfunctionalized compounds with dicarbonyls,[22] we have attempted reaction of 3-(2-hydroxyethyl)- and 3-(2-aminoethyl)-1,3-propanediamines (**1** and **5**) with glyoxal (**2**), affording dioxatetraaza- and hexaazaperhydroperylenes (**4** and **6**), and have predicted one of three possible stereoisomers for **4**, and have determined it by X-ray crystallography. Here we report a one-pot preparation of polyheterocycles and prediction of their stereochemistries using AM1.

RESULTS AND DISCUSSION

The reaction of **1** with one equivalent of **2** was carried out in water at room temperature to give the perhydropyrimidinomorpholine (**3**) and pentaheterocycle (**4**) in 38 and 11 % yields, respectively (Scheme 1). The structure of compound (**3**) was assigned as follows: The mass spectrum showed a molecular ion peak at *m/z* 158, which represented the loss of one molecule of water from each equivalent of



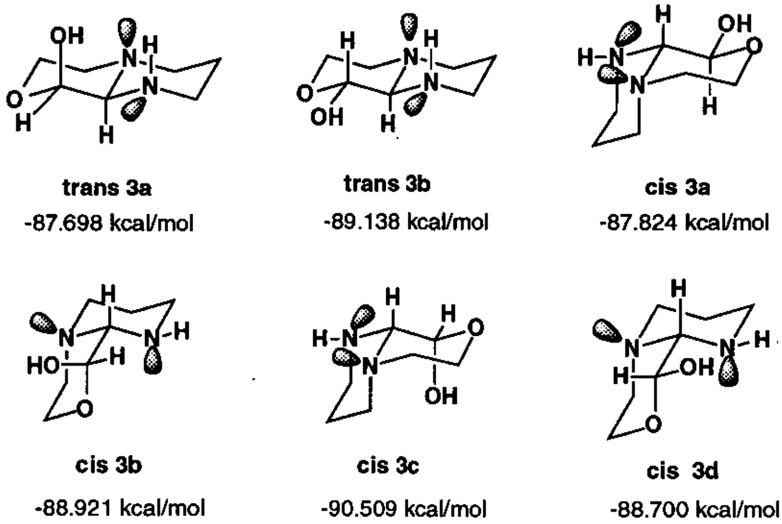
1. 2 3 4

Scheme 1

1 and **2**. The ^{13}C-nmr spectrum indicated a mixture of two compounds consisting of pairs of seven carbons. In the ^{1}H-nmr spectrum, characteristic methine hydrogens on NCHN and OCHO indicated 3 : 1 ratio of stereoisomeric compounds at δ 2.96 and 4.96; 3.81 and 4.56 ppm with J=2.2 and 6.6 Hz, respectively. These values apparently showed the ratio of cis and trans isomers. However, these isomers were not separated by silica gel column chromatography.

To elucidate the stereochemistry of **3**, heats of formation (ΔHf) for the two possible trans and four cis fused stereoisomers shown in Figure 1 were calculated by AM1. From these results, the highest values of ΔHf were -90.51 kcal/mol in cis **3c** and -89.14 kcal/mol in trans **3b**, presumably because these have less steric interaction and the other four possible stereoisomers (trans **3a**, cis **3a**, cis **3b**, and cis **3d**) have 1,3-interactions between lone pairs of hydroxy and oxygen groups (Figure 1).

Figure 1 Heats of Formation (ΔHf) of Trans and Cis Fused Perhydropyrimidinomorpholine (3) by AM1


trans 3a -87.698 kcal/mol

trans 3b -89.138 kcal/mol

cis 3a -87.824 kcal/mol

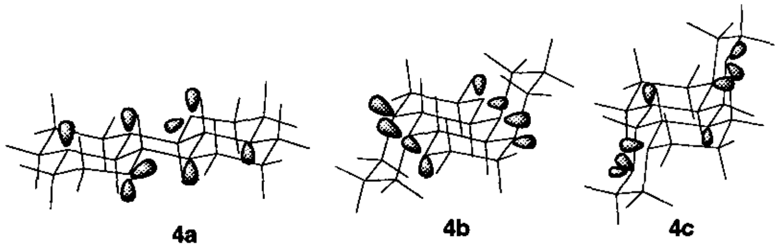
cis 3b -88.921 kcal/mol

cis 3c -90.509 kcal/mol

cis 3d -88.700 kcal/mol

Furthermore, compound (**3**) was converted into **4** in 36% yield by refluxing an aqueous solution in the presence of AcOH as a catalyst. From this result and a molecular ion peak at m/z 280 in the mass spectrum, compound (**4**) was presumed to be a condensed product of two molecules of **3** with the loss of two molecules of water. The ^{13}C-nmr spectrum showed one-half of the total number of expected carbon signals (7 carbons), consisting of five methylene carbons at δ 19.0, 43.9, 49.3, 52.3, and 65.4 and two methine carbons at δ 69.1 and 88.3 ppm. These results are consistent with a structure having a C_2 symmetry axis, which was assigned the 2 : 2 adduct compound (**4**).

Compound (**4**) has three possible stereoisomers, (**4a**, **4b**, and **4c**). To determine which of these is the most stable, their heats of formation (ΔHf) were calculated by a molecular orbital method (AM1).[23] The results are summarized in Figure 2. Compounds (**4a** and **4c**) had the highest (31.07 kcal/mol) and lowest (-35.67 kcal/mol) heats of formation by AM1, respectively. This suggests that the all trans fused form (**4a**) results in 1,3-repulsion between the lone pairs on nitrogens and oxygens, while comparison of the cis-cis fused forms (**4b** and **4c**) indicates that one stereoisomer of **4c** is more stable than that of **4b** by 11.93 kcal/mol. These results were also supported using PM3,[23] which showed a similar tendency, with compound (**4a** and **4c**) having the highest ΔHf -26.7 kcal/mol and lowest -66.94 kcal/mol, respectively.



ΔHf (kcal/mol)		4a	4b	4c
	AM1	31.07	-23.74	-35.67
	PM3	-26.71	-54.48	-66.94

Figure 2 Heats of Formation of All Trans Fused Form (**4a**) and Two Cis-Two Trans Fused Form (**4b**) and (**4c**)

Therefore, the stereochemistry of **4** is most likely given by **4c**, although this stereochemistry was not confirmed by ^{1}H-^{13}C-nmr COSY. Ultimately however, the structure of **4** was determined by X-ray *crystallography and shown to be the trans-cis-trans-trans fused form* (**4c**) *(Figure 3)*.[24]

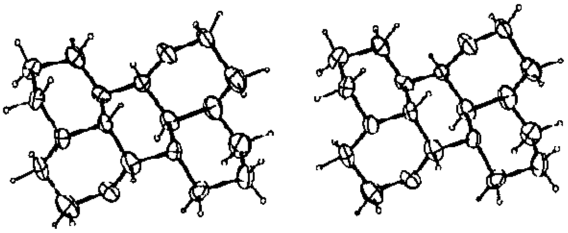


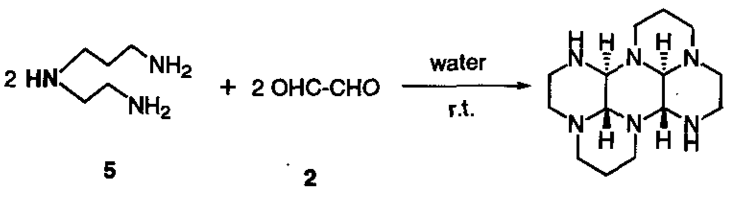
Figure 3 A stereoview of **4c**

Table 1

bond length (Å)	AM1	PM3	X-ray
C3-C4	1.352	1.487	1.450
N4-C4a	1.438	1.500	1.463
O7-C7a	1.402	1.429	1.453
C4a-C7a	1.523	1.553	1.522
bond angle (°)	AM1	PM3	X-ray
N4-C4a-N16	110.7	110.8	111.7
N4-C4a-C7a	109.5	109.1	111.1
O7-C-7a-N8	105.0	106.8	109.3
C4a-N4-C5	107.7	114.5	112.4

A comparison of the bond lengths, bond angles, and dihedral angles of the final coordinates as obtained from AM1, PM3, and X-ray analysis is shown in Table 1.

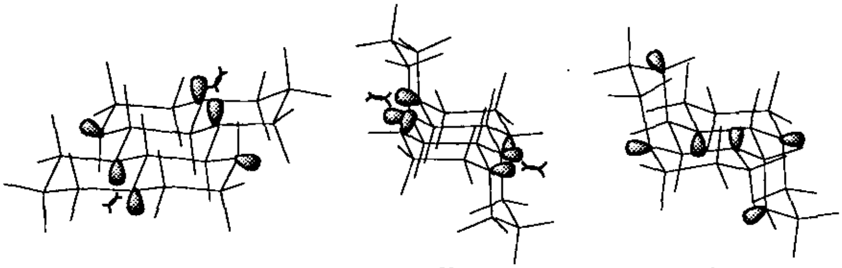
As an extension of this method, we attempted to react **2** with **5**. An aqueous solution of **2** and **5** was stirred for 15 h at room temperature and was worked up in a similar manner to give hexaazaperhydroperylene (**6**) in 39 % yield (Scheme 2). The structure of **6** was determined as follows: The CI-mass spectrum indicated a molecular ion at *m/z* 279 $(M+1)^{+}$. The ^{13}C-nmr spectrum indicated one-half of the total number of



5 **2** **6**

Scheme 2

methine carbons at δ 75.7 and 86.0 ppm, while the ^1H-^{13}C-nmr COSY indicated two characteristic methine signals at δ 2.12 and 2.89 ppm with J=7.0 Hz. These results supported a C_2 symmetrical



6a **6b** **6c**

all trans fused form **69.59 kcal/mol**

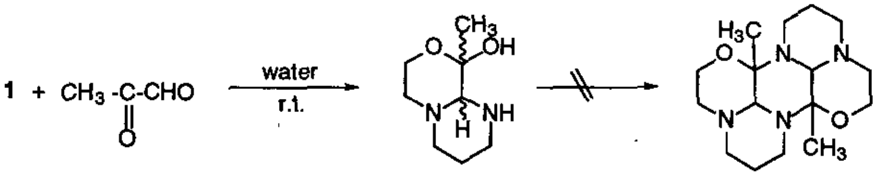
two cis fused form A **68.66 kcal/mol**

two cis fused form B **56.65 kcal/mol**

Figure 4 Heats of Formation for Compound 6 by AM1

structure analogous to that observed with compound (**4**). Compound (**6**) also has three possible stereoisomers, (**6a**, **6b**, and **6c**), whose heats of formation were calculated by AM1. These results are summarized in Figure 4. The all trans fused form (**6a**) had the highest heat of formation (69.6 kcal/mol), while two cis fused forms **6b** and **6c** had ΔHf values of 68.7 and 56.7 kcal/mol, respectively. These values suggest that stereoisomer **6c** is more stable than **6b** by 12.01 kcal/mol due to a lack of repulsion between lone pairs on nitrogens.

Finally the reaction of **1** with pyruvaldehyde (**7**) was performed in water to afford perhydropyrimidino-oxazine (**8**) in 56% yield without producing detectable dimer (**9**) (Scheme 3). Compound (**8**) showed a molecular ion at m/z 173, while the ^{13}C-nmr spectrum showed a pair of eight carbon signals in ratio of 7 : 1. From these data, two stereoisomeric cis / trans fused forms were deduced.



7 **8** **9**

Scheme 3

Conversion of **8** to **9** was attempted by refluxing an aqueous solution containing acetic acid as a catalyst, but no dimeric compound was isolated, and only starting compound was recovered.

Unlike compound **3**, which dimerized smoothly, compound **8**, having a substituent at position 1, is assumed not to undergo intermolecular dimerization, because of steric hindrance.

In conclusion, the polyheterocycles (**4** and **6**) derived from 3-(2-hydroxyethyl)- and 3-(2-aminoethyl)-1,3-propanediamines (**1** and **5**) demonstrate that the cis-fused isomer is formed preferentially in order to avoid 1,3-lone pair interactions. Heats of formation calculated from AM1, and X-ray structure analyses strongly support these results.

EXPERIMENTAL

Melting points were determined with a Yanagimoto micro-melting point apparatus and are uncorrected. Ir spectra were recorded with a JASCO IRA-1 grating ir spectrophotometer. JEOL JNM-EX-270 and GX400 spectrometers were used for both ^{1}H- (270 and 400 MHz) and ^{13}C-nmr (67.5 and 100 MHz) spectra. Mass spectra were obtained with a JEOL JMS-DX303 mass spectrometer.

2-Hydroxyhexahydropyrimidino[1,2-*c*]morpholine (3) and 7,15-Dioxa-4,8,12,16-tetra-azaperhydroperylene (4)

To a stirred solution of **1** (3.55 g, 30 mmol) in water (15 ml) was gradually added **2** (4.35 ml, 30 mmol, 40% w/v in water) at room temperature. The reaction mixture was stirred for 12 h, and saturated with NaCl, extracted with CH_2Cl_2 (6 x 30 ml). The CH_2Cl_2 layer was dried over $MgSO_4$. When the CH_2Cl_2 was evaporated under reduced presssure to one-third volume, the crystals were filtered and recrystallized from AcOEt to give **4**. The filtrate was evaporated under reduced pressure. The resulting solid was recrystallized from EtOH to give **3**.

3: yield 1.8 g (38%); mp 66-68 °C; ir ν 3290 (NH), 3100 (OH) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 1.52 (d, CHH, *J*=13.2 Hz), 1.78-1.93 (m, C$\underline{H}$H), 2.14-2.24 (m, CH$\underline{H}$), 2.33-2.40 (m, C$\underline{H}$H), 2.56-2.68 (m, CH$\underline{H}$), 2.66 (d, NCHN, *J*=2.2 Hz, trans fused), 2.93 (d, C$\underline{H}$H, *J*=2.2 Hz), 3.08-3.15 (m, CH$\underline{H}$), 3.41-3.49 (m, C$\underline{H}$H), 3.81 (d, NCHN, *J*=6.6 Hz,cis fused), 4.21-4.27 (m, CH$\underline{H}$), 4.56 (d, OCHO, *J*=6.6 Hz, cis fused), 4.96 (d, OCHO, *J*=2.2 Hz,trans-fused); ^{13}C-nmr ($CDCl_3$) δ: cis-fused 26.44, 44.08, 53.34, 54.55, 58.56 (CH_2), 76.23, 89.83 (CH); trans-fused 25.05, 44.63, 52.70, 53.86, 63.54 (CH_2), 79.45, 94.96 (CH); EI-ms*m/z* 158 (M^+); *Anal.* Calcd for $C_7H_{14}N_2O_2$: C, 53.14; H, 8.92; N, 17.71. Found: C, 53.48; H, 9.07; N, 17.96.

4: yield 0.9 g (11%); mp 219-221 °C; ir ν 2900 (CH_2) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 1.31 (d, 2 x C$\underline{H}$H, *J*=10.9 Hz), 2.24 (d, 2 x CH$\underline{H}$, *J*=11.0 Hz), 2.30 (d, 2 x C$\underline{H}$H, *J*=11.0 Hz), 2.88-2.98 (m, 3 x CH$\underline{H}$), 3.18 (dd, 2 x C$\underline{H}$H, *J*=11.9, 9.4 Hz), 3.41 (dd, 2 x CH$\underline{H}$, *J*=11.9, 8.4 Hz), 3.65 (t, 2 x C$\underline{H}$H, *J*=11.4 Hz), 3.97-4.06 (m, 3 x C$\underline{H}$H), 4.07 (s, 2 x C$\underline{H}$H); ^{13}C-nmr ($CDCl_3$) δ 19.04, 43.93, 49.27, 52.31, 65.54 (CH_2), 69.13, 88.34 (CH); EI-ms *m/z* 280 (M^+); *Anal.* Calcd for $C_{14}H_{24}N_4O_2$: C, 59.98; H, 8.63; N, 19.98. Found: C, 59.87; H, 8.69; N, 20.07.

4,7,8,12,15,16-Hexaazaperhydroperylene (6)

To a stirred solution of **5** (1.2 ml, 10 mmol) in water (15 ml) was gradually added **2** (1.45 ml, 10 mmol, 40% w/v in water) under cooling with ice and water. The reaction mixture was stirred at room temperature for seven days. The aqueous solution was saturated with NaCl and extracted with CH_2Cl_2 (6 x 30 ml). The CH_2Cl_2 layer was dried over $MgSO_4$. Removal of the CH_2Cl_2 afforded a residue, which was recrystallized from acetonitrile to give **6**. yield 1.1 g (39%); mp 265-267 °C; ir ν 3250 (NH) cm^{-1}; ^1H-nmr ($CDCl_3$) δ 0.92 (br, 2 x NH), 1.59 (d, 2 x C$\underline{H}$H, *J*=12.5 Hz), 1.77 (t, 2 x CH$\underline{H}$, *J*=11.7 H), 1.81-1.92 (m, 2 x C$\underline{H}$H), 2.02-2.10 (m, 2 x CH$\underline{H}$), 2.12 (d, 2 x NCHN, *J*=7.0 Hz), 2.74 (d, 2 x C$\underline{H}$H, *J*=11.7 Hz), 2.85-2.90 (m, 4 x CH$\underline{H}$), 2.89 (d, 2 x NCHN, *J*=7.0 Hz), 2.96 (d, 2 x C$\underline{H}$H, *J*=6.2 Hz), 3.75 (d, 2 x CH$\underline{H}$, *J*=11.0 Hz); ^{13}C-nmr ($CDCl_3$) δ 24.04, 43.47, 48.76, 54.61, 56.31 (CH_2), 75.68, 85.97 (CH); CI-ms *m/z* 279 $(M+1)^+$; *Anal.* Calcd for $C_{14}H_{26}N_6$: C, 60.40; H, 9.41; N, 30.19. Found: C, 60.24; H, 9.33; N, 29.87.

2-Hydroxy-2-methylhexahydropyrimidino[1,2-*c*]morpholine (8)

To a stirred solution of **1** (1.77 g, 15 mmol) in water (15 ml) was gradually added **7** (2.7 ml, 15 mmol, 40% w/v in water) at room temperature. The reaction mixture was stirred for 12 h, and saturated with NaCl, extracted with CH_2Cl_2 (7 x 30 ml). The CH_2Cl_2 layer was dried over $MgSO_4$. When the CH_2Cl_2 was evaporated under reduced presssure, crystals separated were collected, washed with Et_2O, and recrystallized from isopropyl ether to give **8**. yield 1.7 g (66%); mp 106 °C; ir ν 3300 (NH), 3120 (NH) cm^{-1}; ^1H-nmr ($CDCl_3$) δ 1.41 (s, CH_3), 1.52 (d, C$\underline{H}$H, *J*=13.2 Hz), 1.71 (dt, CH$\underline{H}$, *J*=12.8, 4.2 Hz), 2.26 (td, C$\underline{H}$H, *J*=12.1, 2.9 Hz), 2.41 (td, CH$\underline{H}$, *J*=12.1, 3.7 Hz), 2.54 (dd, C$\underline{H}$H, *J*=11.7, 1.8 Hz), 2.63 (td, CH$\underline{H}$, *J*=13.2, 2.7 Hz), 2.83 (s, CH), 2.94 (d, C$\underline{H}$H, *J*=11.4 Hz), 3.11 (dd, CH$\underline{H}$, *J*=13.9, 4.4 Hz), 3.55 (dd, C$\underline{H}$H, *J*=11.7, 2.9 Hz), 4.06 (td, CH$\underline{H}$, *J*=12.1, 2.9 Hz), 4.10 (br, OH); ^{13}C-nmr ($CDCl_3$) δ cis fused 23.01 (CH_3), 25.26, 52.70, 52.83, 59.23, 68.49 (CH_2), 90.07 (CH), 93.90 (-C-); trans fused 19.76 (CH_3), 43.35, 51.82, 59.80, 67.33 (CH_2), 94.41 (CH), 93.90 (-C-); CI-ms *m/z* 173 $(M+1)^+$; *Anal.* Calcd for $C_8H_{16}N_2O_2$: C, 55.79; H, 9.36; N, 16.27. Found: C, 55.45; H, 9.28; N, 16.03.

X-Ray Analysis 4 --- Single crystals of $C_{14}H_{24}N_4O_2$ corresponding to **4** were prepared by allowing an ethanol solution of the compound to stand for about 3 weeks. Their crystallographic data were collected as follows: Crystal Data triclinic, space group P1, a=8.123 (5), b=9.341 (6), c=5.015 (2), α=87.56 (5), β=105.60 (4) γ=112.82 (5) v= 337.0 (4), Z=1, R final 0.0549 (number of RD 1080, Fo>3.0σF)

Crystal Data --- The cell constants were determined from least-squares procedure using the value of the Bragg angles of 20 reflections measured on a RIGAKU AFC-6 four-circle autodiffractometer equipped with a graphite monochromatic Mo-Ka source, which is was interfaced to a PANAFACOM U-1200 minicomputer. The space groups were selected from systematic absences and the number of molecules per unit cell, and were later confirmed in the course of the subsequent structure refinement. Intensity data were collected in the range of $2\theta < 55°$ using the ω-2θ scan technique. A variable scan rate was adopted. Reflection was monitored after every measurement of 100 reflections. Of the1412 independent reflections for **4**, 1080 was treated as observed (Fo>3.0σF), respectively. The intensities were corrected for Lorentz and polarization effects, but no correction was applied for absorption.

Structure solution and refinement --- An overall temperature factor obtained from a Wilson plot gave the correct solution. The structure was solved by the direct method using the MULTAN78 series of programs.[25] An E map calculated with using the signed E's (E>1.2) revealed the positions of all of the expected non-hydrogen atoms. Refinements were carried out by the block-diagonal least-square least-squares method. Six cycles of isotropic refinement and six cycles of anisotropic refinement led to a an R index. All of the hydrogens were located at the calculated positions. After adding the hydrogens, but keeping their positional and thermal parameters fixed [B(H)=B(C)+1.0], and refining, we obtained a final R value. All structure-solving programs and the drawing program (ORTEP)[26] were from the Computer Center of Kumamoto University with the Universal Crystallographic Computation Program System (UNICS III).[27]

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