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Configurational Properties of Eight-membered Rings Containing Two Ketenimine Units†

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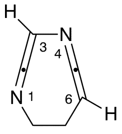
AMI semi-empirical SCF MO calculations for diastereoisomeric forms of 1,4-, 1,6-, and 3,4-diazacycloocta-1,2,4,5-tetraene and 1,5- and 1,7-diazacycloocta-1,2,5,6-tetraene are reported for ten configurations and two transition-state geometries for configurational interconversions.

Monocyclic medium rings containing two ketenimine moieties are strained compounds with two stereogenic centres and should exist in two diastereoisomeric forms, one diastereoisomer being racemic and the other a *meso* compound. While the structural properties of cyclic allenes[1] have been studied both experimentally[2,3] and theoretically,[3,4] there are only few reports concerning synthesis and conformational features of cyclic ketenimines.[5]

Recently, we reported[6] AM1 SCF MO calculations for conformational and configurational energy surfaces of nine-membered rings containing two adjacent ketenimine moieties. We now present a detailed AM1 study of the ground-state geometries and two transition states for configurational interconversions in eight-membered rings containing two ketenimine units **1**–**5**. Even though compounds **1**–**5** are not presently available for more studies, it is possible to learn something about them by using theoretical methods that have been proved to be reliable in other applications. AM1 is one of the most reliable semi-empirical methods known for calculating various structural aspects of organic molecules.[7]



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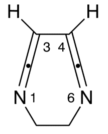

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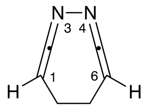

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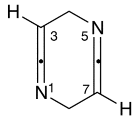

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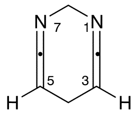

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Calculations

Semi-empirical calculations were carried out using the AM1 method with the MOPAC 6.0 program[8] implemented on a VAX 4000-300 computer. Energy-minimum geometries were located by minimizing energy with respect to all geometrical coordinates, and without imposing any symmetry constraints. The structures of the transition-state geometries were obtained using the optimized geometries of the equilibrium structures according to the procedure of Dewar *et al.*[9] (keyword SADDLE). All structures were characterized as stationary points, and true local energy-minima and transition-states on the potential energy surface were found using the keyword FORCE. All energy-minima and transition-state geometries obtained in this work are calculated to have $3N-6$ and $3N-7$ real vibrational frequencies, respectively.[10]

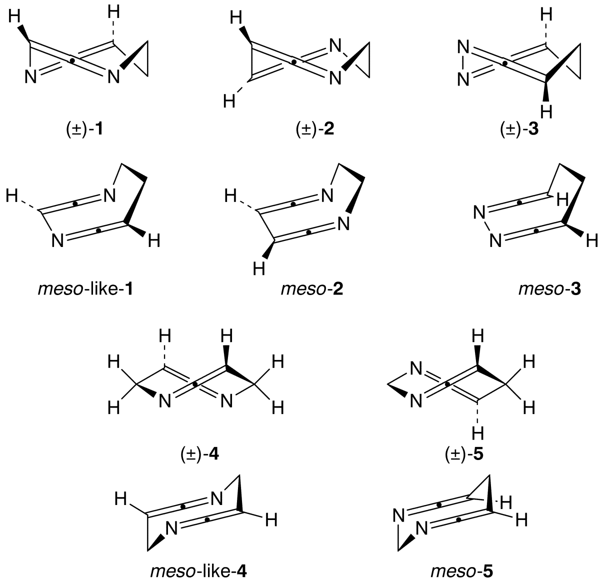

Fig. 1 Ten possible diastereoisomers of compounds **1**–**5**

Results and Discussion

The result of AM1 calculations for compounds **1**–**5** are shown in Table 1 and Fig. 1. The (±)-isomer is found to be the most stable diastereoisomer for these compounds. The *meso*- (or *meso*-like-) isomer[11] is 5.2–36.6 kJ mol^{-1} less stable than the corresponding (±)-isomer. The two diastereoisomers of compounds **1**–**5** are conformationally rigid. However, configurational interconversion between the two sets of diastereoisomers is possible for compounds **1** and **2**. The calculated strain-energy barrier for this process is 53.8 and 66.8 kJ mol^{-1} for **1** and **2**, respectively. This interconversion may proceed through expansion of $\theta C_{sp^3}{-}N{-}C_{sp^2}$ to about 144–146°, *via* in-plane inversion at the nitrogen atom (see Table 1 and Fig. 2). Rotation about the C=N and C=C bonds requires more than 200 kJ mol^{-1} energy. Thus, according to the these calculations, compounds **1** and **2** are expected to be configurationally flexible at room temperature.

The *meso*-like isomer of **1** is twisted around the C–CH$_2$–CH$_2$–C torsional angle by about 20°. The envelope conformation ($\phi_{6781}=0$) is calculated to be 1.8 kJ mol^{-1} less stable than the twist-envelope geometry. However, the

[(±)-**1** ⇌ *meso*-like-**1**]‡ [(±)-**2** ⇌ *meso*-**2**]‡

Fig. 2 Calculated transition-state geometries for configurational interconversion of the two sets of diaseteroisomers of **1** and **2**

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Calculated heats of formation (kJ mol^{-1}) and selected structural parameters (bond angles θ and dihedral angles ϕ in °) for *meso*- and (±)-isomers of **1**–**5**

	1			**2**			**3**		**4**		**5**	
Feature	(±)	*meso*-like	TS	(±)	*meso*	TS	(±)	*meso*	(±)	*meso*-like	(±)	*meso*
ΔH_f°	521.2	528.6	575.0	493.8	520.2	560.6	584.4	589.6	477.3	507.7	474.8	511.4
$\Delta\Delta H_f^{\circ\,a}$	0.0	7.4	53.8	0.0	26.4	66.8	0.0	5.2	0.0	33.4	0.0	36.6
θ_{123}	158	159	161	162	163	164	161	157	168	169	167	168
θ_{234}	112	115	112	110	113	115	111	116	116	117	118	119
θ_{345}	110	114	115	110	113	109	111	116	116	113	114	109
θ_{456}	165	161	164	162	163	166	161	157	116	117	118	116
θ_{567}	121	118	120	122	121	144	120	120	168	169	167	168
θ_{678}	112	112	112	114	115	114	111	112	119	117	118	119
θ_{781}	113	115	112	114	114	115	111	112	111	105	114	109
θ_{812}	122	123	146	122	120	120	120	120	119	117	118	116
ϕ_{1234}	10	–27	–11	16	8	–2	–49	–12	37	–49	–58	–59
ϕ_{2345}	–39	6	–21	35	0.0	–20	–49	0.0	–36	52	27	60
ϕ_{3456}	–17	–12	–29	18	–12	4	–49	11	–26	–52	24	–52
ϕ_{4567}	83	68	34	–83	67	–8	55	52	37	49	–9	–4
ϕ_{5678}	–71	–56	–75	66	–61	7	–72	–71	32	9	–60	62
ϕ_{6781}	64	–20	45	–58	–6	32	72	–2	–26	–60	27	–61
ϕ_{7812}	–67	76	–11	66	70	–72	–72	73	26	60	25	52
ϕ_{8123}	56	–31	16	–81	–63	66	55	–51	32	–9	–11	0.0
ϕ_{8134}	60	50	60	–60	–52	60	64	–58	66	–55	–65	56
ϕ_{3467}	62	–55	2	–60	52	–3	64	58	—	—	—	—
ϕ_{4578}	—	—	—	—	—	—	—	—	66	55	–65	–56

[a] Relative to the best configuration of each compound.

torsional energy is greatly reduced upon twisting and this more than makes up the concomitant increase in the internal angle strain. This twisting from symmetrical envelope conformation is about 6° and 2° in **2** and **3**, respectively.

The C=C=N bond angles are bent in all geometries of **1**–**3** and they are about 15–23° more compressed than those found in acyclic ketenimines.[12] Also the ϕ_{8134} and ϕ_{3467} torsional angles in ketenimine moieties of all isomers of **1**–**3** are fairly twisted from their energy-minima at 90° as a result of ring strain (see Table 1).

The most stable diastereoisomer among ten possible isomers of **1**–**5** is the axial symmetrical (±)-configuration of **4**. Configurational interconversion of the two diastereoisomers of **3–5** may proceed through inversion at nitrogen or rotation about C=C or C=N bonds. All of these mechanisms are calculated as high energy processes and need more than 200 kJ mol^{-1}. Thus, the two sets of diastereoisomers of **3**–**5** are expected to be configurationally stable at room temperature.

Important structural parameters for the two geometries of **4** and **5** are given in Table 1. The C=C=N bond angles are slightly bent in all geometries and they are 11–13° more compressed than those found in acyclic ketenimines.[12]

In summary, AM1 calculations provide a picture of configurations of eight-membered ring diketenimines **1**–**5** from both structural and energetic points of view. The (±)-diastereoisomer of **1**–**5** is calculated to be more stable than the *meso*- (or *meso*-like-) isomer. Configurational isomerization of the two diastereoisomers of **3**–**5** are high energy processes with a barrier about 200 kJ mol^{-1}. However, configurational interconversion between the two sets of diastereoisomers of **1** and **2** requires *ca.* 54 and 67 kJ mol^{-1}, respectively.

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