

AM1 study of the conformational properties of bicyclo[3.3.3]undecane and its *N*-bridgehead derivatives[†]

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AM1 semiempirical SCF MO calculations show that the BC conformation is the most stable form of bicyclo[3.3.3]undecane (**1**) and its *N*-bridgehead derivatives (**2** and **3**), whereas the corresponding BB conformations are calculated to be from 4.3 kcal/mol in (**3**) to 7.1 kcal/mol in (**1**) higher in energy.

Keywords: conformational properties, bicyclo [3.3.3] undecane

Bicyclo[3.3.3]undecane (manxane) (**1**) and its *N*-bridgehead derivatives (**2** and **3**) are interesting compounds with regard to their possible conformational relationship to eight-membered rings in the carbocyclic series, and when one or more ring atoms are replaced by heteroatoms.

Compound (**2**), with a C_3 axis, is of special interesting in that it represents an unsubstituted[3.3.3] ring system capable of existing in enantiomeric forms if the conformational energy barrier is sufficiently large.

Although the parent compound (**1**) and some of its derivatives have been the subject of various investigations,^{1,2} there is at present no semiempirical SCF MO study of the structure or conformational properties of these compounds. As pointed out in a recent paper,³ there are various pathways for conformational interconversion in (**1**). We wish to report a detailed AM1 (Austin Model 1) SCF MO study of the conformational properties of **1–3**.

Altogether five geometries were found for a description of the conformational feature of compounds **1–3**. Two correspond to energy minima, and three to one dimensional energy maxima (saddle points or transition states) as shown in Fig. 1.

The heats of formation for various molecular geometries of compounds **1–3** calculated by the AM1 method are given in Table 1.

The mechanism of bridge flipping is certainly stepwise and presumably proceeds as shown in Fig. 1, with the rate-limiting step being the first.

The calculated strain-energy barrier for this process in (**1**) is 11.8 kcal/mol. The calculated strain-energy barrier is decreased when heteroatoms (nitrogen) are included in a bridgehead positions. Conformational barriers in compounds **2** and **3** are calculated to be 7.8 and 7.0 kcal/mol, respectively.

In conclusion, AM1 calculations provides a fairly clear picture of the conformational properties of (**1–3**). The replacement of carbon by nitrogen in the bridgehead position produces no changes in the conformational interconversion but there is obviously lowering of the conformational barriers. The reasons for this are connected with the strain increase as the intrabridgehead distance ($d_{1,5}$) increases in the transition state (TS1) correspond to these compounds (see Table 1). The calculated barrier for BC to BC interconversion for manxane (11.8 kcal/mol) is in good agreement with molecular mechan-

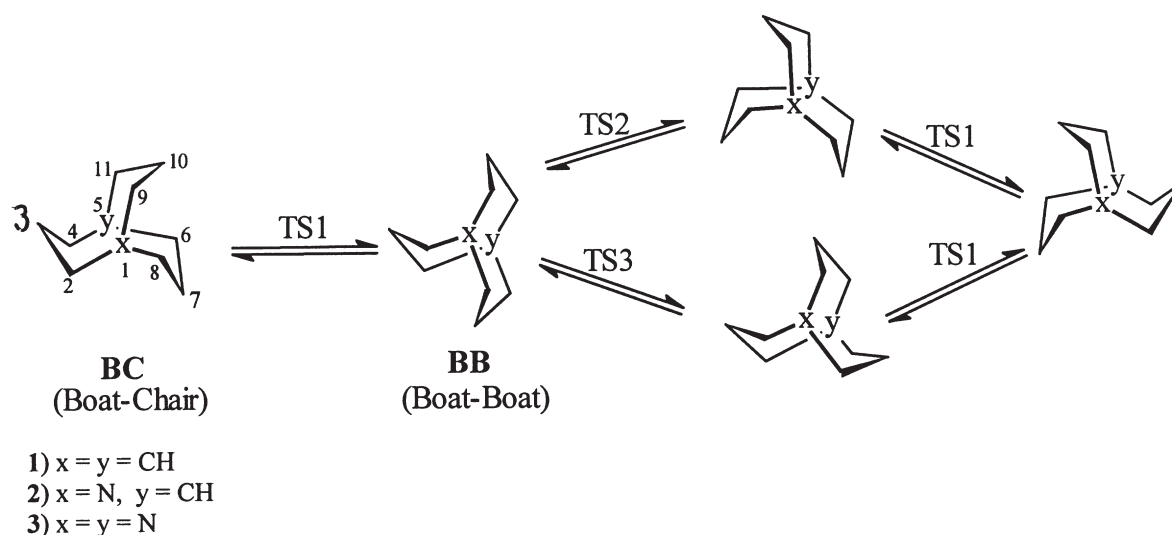


Fig. 1 Various pathways for BC to BC interconversion.

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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Calculated heats of formation (kCal mol⁻¹) and selected structural parameters (bond angles θ and dihedral angles Φ in degrees) for compounds **1-3**.

Feature	1					2					3				
	BC (C _{3h})	BB (C _S)	TSI (C _S)	TSII (C _S)	TSIII (C _S)	BC (C ₃)	BB (C ₁)	TSI (C ₁)	TSII (C ₁)	TSIII (C ₁)	BC (C _{3h})	BB (C _S)	TSI (C _S)	TSII (C _S)	TSIII (C _S)
ΔH_f°	-41.1	-34.0	-29.3	-30.8	-26.5	-20.9	-15.1	-13.1	-12.3	-7.7	-0.9	3.4	6.1	5.7	10.1
$\Delta\Delta H_f^\circ$	0.0	7.1	11.8	10.3	14.6	0.0	5.0	7.8	8.6	13.2	0.0	4.3	7.0	6.6	11.0
d_{15} (Å ^o)	4.5	3.3	3.3	3.3	3.2	3.2	3.1	3.1	3.2	3.1	3.1	3.0	3.0	3.0	3.5
$\theta_{1,2,3}$	118	121	118	126	120	119	122	110	124	120	119	121	119	124	120
$\theta_{1,9,10}$	118	117	126	117	120	119	119	125	118	119	119	121	123	118	120
$\theta_{2,3,4}$	117	117	114	128	116	116	119	115	126	114	115	118	114	125	116
$\theta_{2,1,8}$	114	114	113	115	107	116	117	118	117	118	117	119	118	118	118
$\theta_{2,1,9}$	114	118	116	115	118	116	119	118	117	119	117	119	118	118	120
$\theta_{3,4,5}$	118	121	118	126	120	118	119	117	126	119	119	121	119	124	120
$\theta_{4,5,6}$	114	114	113	115	107	114	116	117	115	112	117	119	118	118	118
$\theta_{4,5,11}$	114	118	116	115	118	114	115	113	117	121	117	119	118	118	120
$\theta_{5,6,7}$	118	117	118	117	124	118	118	118	117	124	119	118	118	118	123
$\theta_{6,5,11}$	114	112	114	114	107	114	113	113	113	113	117	118	118	119	118
$\theta_{6,7,8}$	117	114	114	114	126	116	113	113	114	125	115	118	114	114	123
$\theta_{7,8,1}$	118	117	118	117	124	119	119	119	118	124	119	118	118	118	123
$\theta_{8,1,9}$	114	112	114	114	107	116	117	118	118	118	117	118	118	119	118
$\theta_{9,10,11}$	117	117	128	114	116	116	118	127	114	117	115	118	125	114	116
$\theta_{10,11,5}$	118	117	126	117	120	118	121	124	118	123	119	121	123	118	120
$\Phi_{1,2,3,4}$	71	54	70	0	59	-65	-42	-60	8	-42	61	46	59	0	49
$\Phi_{11,10,9,1}$	71	60	0	71	59	-65	65	6	77	60	61	-49	0	-61	-48
$\Phi_{10,9,1,2}$	-98	-40	-66	-38	-39	100	35	67	-61	43	-101	-53	-75	-50	-55
$\Phi_{5,4,3,2}$	-71	-54	-70	0	-59	68	59	134	5	72	-61	-46	-59	0	-49
$\Phi_{3,2,1,9}$	36	42	40	67	39	-43	-57	-53	69	-65	44	54	50	77	55
$\Phi_{6,5,4,3}$	98	92	96	68	98	-99	-95	-97	-70	-115	101	97	101	76	105
$\Phi_{11,5,4,3}$	-36	-42	-40	-67	-39	35	40	37	-70	22	-44	-54	-50	-77	-55
$\Phi_{7,6,5,4}$	-36	-38	-33	-39	-98	35	20	76	24	53	-44	-46	-44	-49	-79
$\Phi_{10,11,5,4}$	98	40	66	38	39	-99	-60	-79	24	-48	101	53	75	50	55
$\Phi_{8,7,6,5}$	-71	-70	-74	-71	0	68	77	76	-57	9	-61	-62	-62	-62	0
$\Phi_{5,11,10,9}$	-71	-60	0	-71	-59	68	-40	8	-57	-43	-61	49	0	61	48
$\Phi_{6,7,8,1}$	71	70	74	71	0	-65	-48	-56	77	14	61	62	62	62	0
$\Phi_{6,5,11,10}$	-36	-100	-71	-98	-98	35	76	58	-113	88	-44	-99	-77	-103	-104
$\Phi_{7,8,1,9}$	-98	-99	-104	-98	-71	100	86	97	86	59	-101	-105	-107	-103	-80
$\Phi_{7,8,1,2}$	36	38	33	39	98	-43	-64	-56	-86	-95	44	46	44	49	79
$\Phi_{7,6,5,11}$	98	99	104	98	71	-99	-116	-113	86	-87	101	105	107	103	80
$\Phi_{8,1,9,10}$	36	100	71	98	98	-43	-115	-86	-113	-111	44	99	77	103	104
$\Phi_{8,1,2,3}$	-98	-92	-96	-68	-98	100	92	100	-78	89	-101	-97	-101	-76	-105

ics calculations (12.0 kcal/mol).³ On the other hand, this barrier for compound **3** (7.0 kcal/mol) is in good agreement with the experimental data (6.9 kcal/mol) that reported for this compound.⁴⁻⁶

Calculations

Initial estimates of the geometries of structures **1-3** were obtained by molecular-mechanics program PCMODEL (88.0)⁷ followed by full minimisation using the semiempirical AM1 method⁸ in the MOPAC 6.0 computer program,^{9,10} implemented on a VAX 4000-300 computer. Optimum geometries were located by minimising energy, with respect to all geometrical coordinates, and without imposing any symmetry constraints.

The structure of the transition-state geometries were obtained using the optimized geometries of the equilibrium structures according to the procedure Dewar *et al.*¹¹ (keyword SADDLE). All geometries were characterised as stationary points, and true local energy minima and transition states on the potential energy surface were found using 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.¹²

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