Investigation of the Mechanism of *syn–anti*-Isomerism in Imines using CNDO/2 Calculations[1]

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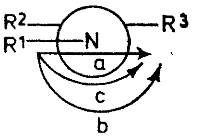
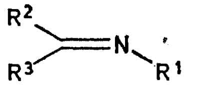
Summary Barriers to *syn–anti*-isomerism *via* torsion about the C=N double bond and *via* inversion at imino-nitrogen obtained using CNDO/2 calculations indicate that the lowering of the barrier by heteroatoms attached to the imino-carbon atom is a reflection of a torsional contribution of the mechanism.

THE mechanism of *syn–anti*-isomerism in imines has generated considerable interest recently.[2] Three possible mechanisms have been discussed: (a) inversion at imino-nitrogen *via* a transition state with *sp* hybridization at nitrogen, (b) torsion about the imino-double bond, and (c) an intermediate mechanism which has torsional and inversional components. The three mechanisms, schematically represented in Newman projection (1), differ in the magnitude of the CNR[1] angle at the transition state; 180° in (a), 120° in (b), and intermediate between these two extremes in (c).



(1)



	R1	R2	R3
(2)	H	H	H
(3)	H	H	OH
(4)	H	NH_2	NH_2

Marullo and Wagener[3] have demonstrated that heteroatoms, with lone pairs of electrons, bonded to the imino-carbon atom substantially lower the barrier to *syn–anti*-isomerization. This finding provided cogent evidence in favour of a torsional contribution to the mechanism (b or c). However, more recent experimental findings have been incompatible with a pure torsional mechanism (b)[2] and have suggested the possibility that the effect of heteroatoms might, in fact, be compatible with an inversion mechanism (a).[4]

Prompted by this possibility, we have examined the effect of heteroatoms on barriers to both inversion and torsion using CNDO/2 SCF–MO calculations.[5] We chose three model molecules for our initial study,‡ formaldimine ($CH_2=NH$, **2**), hydroxyformaldimine ($HOCH=NH$, **3**), and guanidine [$(NH_2)_2C=NH$, **4**]. Formaldimine represents the simplest structure containing the imine functionality, and serves as a basis for comparison with (**3**), which has a single oxygen, and (**4**) which has two nitrogen atoms attached to the imino-carbon atom. In addition, since the inversion and rotation barriers for (**2**) have been obtained using *ab initio* SCF–MO calculations,[6] we are able to compare our results with those obtained using this more rigorous method. The barriers for torsion and inversion for (**2**), (**3**), and (**4**) are given in the Table. The barriers for (**2**) calculated using the CNDO/2 method are in good agreement with those previously obtained by *ab initio* calculations [*viz.*, $\Delta G^‡$ (torsion) = 57 kcal mol^{-1} and $\Delta G^‡$ (inversion) = 26—28 kcal mol^{-1}][6].

The calculation for (**3**) reveals that the presence of the oxygen atom lowers the torsional barrier substantially (by 10 kcal mol^{-1}) while the inversion barrier is nearly unchanged. This effect is more marked for (**4**). The torsional barrier is decreased by 33 kcal mol^{-1} while the inversion barrier is increased by 5 kcal mol^{-1}. While π-bond orders and dipole moments obtained by CNDO/2 may not be quantitatively accurate, the trends in these parameters can offer some insight into the factors responsible for the trends in total energy. As indicated by the data in the Table, π-overlap is diminished by torsion while

Calculated energies, bond orders, and charges

Compound	Geometry[a]	CNH angle (°)	C–N bond length (Å)	Relative energy[b] (kcal mol^{-1})	Bond orders[c] C=N	C–O C–N	Charge on nitrogen	Dipole moment (D)
(**2**)	GS	120	1·26	0	1·00	—	−0·16	1·92[d]
	TS_I	180	1·26	31·1	1·00	—	−0·25	0·82
	TS_T	120	1·29	61·1	0·82	—	−0·37	1·97
(**3**)	GS	120	1·29	0	0·95	0·30	−0·25	2·84
	TS_I	180	1·26	31·8	0·95	0·29	−0·33	1·70
	TS_T	120	1·29	50·7	0·74	0·40	−0·43	3·68
(**4**)	GS	120	1·31	0	0·80	0·40	−0·40	4·30
	TS_I	180	1·31	36·1	0·83	0·39	−0·49	1·93
	TS_T	120	1·32	28·4	0·54	0·50	−0·55	4·91

[a] GS, ground state; TS_I, inversional transition state; TS_T, torsional transition state.
[b] Energies are expressed relative to a ground state energy of zero.
[c] Bond orders for p_z–p_z π-overlap.
[d] Value calculated by *ab initio* method[6] 2·50D. Experimental value for $CH_2=NMe$; 1·53 ± 0·02 D. (K. V. L. N. Sastry and R. F. Curl, *J. Chem. Phys.*, 1964, **41**, 77.)

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† For the purposes of these calculations we assumed sp^2 geometry at the imino-carbon atom in all three molecules and for the amino-nitrogen atoms in (**4**). The ground-state geometry of the imino-nitrogen atoms was also assumed to be that resulting from sp^2 hybridization. An HOC bond angle of 108° was used for (**3**). Bond lengths used were as follows: C–H, 1·09; N–H, 1·03; C–NH_2, 1·35; C–O, 1·368, and O–H, 0·97 Å. The imino-bond length was varied from 1·25—1·35 Å and the length corresponding to the minimum energy was used. In all cases, a singlet configuration was assumed.

it is relatively unaffected by inversion. However, substantial π-bonding occurs even at the transition state for torsion and hence the analogy between torsion about the imine double bond and that about a carbon–carbon double bond is not strictly valid. Although the amount of π-bonding in the imino bond is less in the two molecules with heteroatoms attached to the imino-carbon, the results indicate that the decrease in π-bond order upon torsion is even greater. This decreased bond order is partially, but not completely, compensated for by substantial overlap with the lone pairs of electrons on the other heteroatoms attached to the imino-carbon atoms. This compensation in guanidine is greater than that in hydroxyformaldimine leading to a greater reduction in the torsional barrier.

Examination of either the total dipole moment or the charge on the nitrogen atom reveals trends which are in agreement with the trends in π-overlap. In all three cases the charges on the nitrogen atom are greater in the torsional transition state than in the ground state or the inversional transition state, confirming the judgment that torsion involves a more polar transition state. However, these changes are far less than those which would occur were there a full formal negative charge on the nitrogen atom. In fact, the increased negative charge on nitrogen amounts to less than 0·2 even for guanidine. If these trends in charges and dipole moments accurately reflect the experimental situation we might not expect much of a diminution of the torsional barrier in polar solvents, although some might occur.

Although the barrier calculated for guanidine is substantially higher than the experimentally obtained barriers for substituted guanidines, these results put on a firmer basis the idea that the effect of heteroatoms on the *syn–anti*-isomerization barrier in imines is a reflection of a torsional contribution to the transition state.

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[1] For previous part in this series on stereochemistry at tervalent nitrogen, see M. Raban, F. B. Jones, jun., E. H. Carlson, E. Banucci, and N. A. LeBel, *J. Org. Chem.*, 1970, **35**, 1496.

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