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THERMAL ISOMERIZATION ABOUT DOUBLE BONDS

ROTATION AND INVERSION

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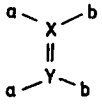
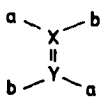
Exactly 100 years ago van't Hoff and Le Bel discovered the existence of stereoisomerism[1]. During the succeeding century a huge number of publications appeared where the two isomers of ethylenes and related structures and their mutual interconversion have been detected and studied.[2,3] Below we will consider the possible mechanism of the thermal isomerization about such classical $p_\pi p_\pi$-double bonds.

The definition of double bond isomers follows the proposal of Blackwood *et al.*[4] where a and b at each central atom (X, Y) are assigned in accordance with the Cahn–Ingold–Prelog–Sequence rules.[5] The



Z



E

techniques of detection and measurement of fast isomerizations have been improved during the last decades. The classical chemical equilibration is now extended by other physical methods such as dynamic NMR measurements (DNMR)[6-8] flash photolysis[9] and ultra-sonic absorption measurements.[10] Besides these experimental methods there exist calculations of *Z,E*-isomerization barriers, both *ab initio* calculations and semiempirical treatments.[11-13] DNMR-measurements and calculations allow the determination of barriers also for degenerated isomerizations (topomerizations[14]).

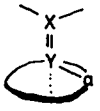
Mechanisms are arrived at empirically from the interpretation of "substituent effects". The dependence of rates or thermodynamic activation parameters* on substituents has to fit the "best" mechanism. Therefore, interpretations often are limited to special cases or are somewhat arbitrary.

*Very often only free enthalpies of activation ΔG^* at different temperatures are known. As long as the temperature range is not too large ΔG^* values can be used for comparison in the first approximation. See also Ref 3.

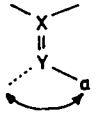
The principle of maximum overlap requires a coplanar arrangement of all ligands at a double bond in the ground state. Considering only the geometric motion of ligands during a thermal *Z,E*-isomerization, we can distinguish the following mechanistic pathways:

1. *Rotation*: The ligand follows an orbit about the X–Y-double-bond axis (A). The transition state is nonplanar (c_1-symmetry).

2. *Inversion*:[15] The ligand moves in the plane of the double bond (B). The transition state involves a planar molecule with linear arrangement X–Y-a (c_{2v}-symmetry). Inversion requires only *one* ligand at Y and a bent ground state structure relative to XY (v.i.).

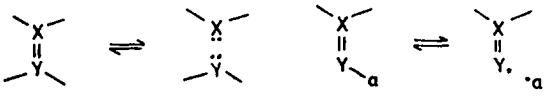


A



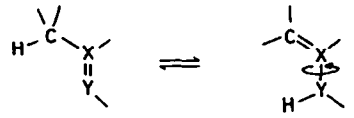
B

3. *Dissociation-Recombination*: The cleavage of the double bond (C) or of the Y-bond to the ligand (D) followed by a recombination has been observed for isomerization of dimeric nitroso compounds[16] and some O-alkyl oximes.[17] These mechanisms are limited to special cases and will not be considered further.



C D

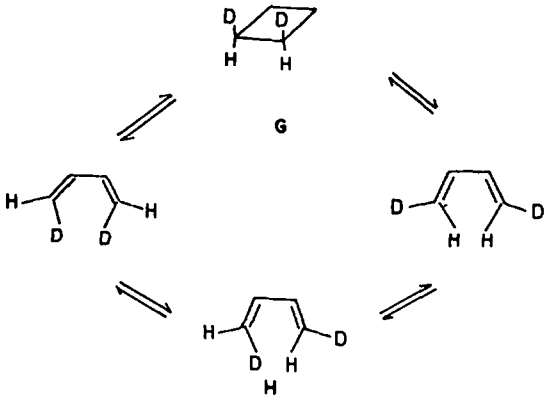
4. *Tautomerization and catalysis*: Tautomerization E,F (e.g. of hydrazones or oximes) as well as addition of a cayalyst may lead to an Z–Y-single bond. Such intermediates allow a fast isomerization. This mechanism has been proved for a hydrazone, comparing the H–D-exchange rates of the α-hydrogens and *Z,E*-topomerization barriers.[18]



OF E O

Many different species can act as catalysts, e.g. metal ions,[19] enzymes,[20] nitrogen dioxide,[21] acids[18,22] and others.[23] In some cases π-complexes and rearrangements to σ-complexes followed by rotation about the X–Y-bond are involved.[19]

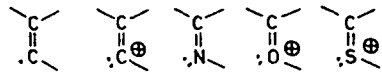
5. Dideutero-1,3-butadiene isomerizes faster by an electrocyclic ring closure to cyclobutene (G) then by direct double bond rotation (H).[24] It remains to be proven if such a mechanism occurs more generally.



Upon focussing our interest on the noncatalyzed thermal† unimolecular isomerization, we were interested in criteria for distinguishing between rotation and inversion.

Rotation involves the loss of π-bond energy while the molecule is in the transition state. Therefore, in the first approximation the thermal isomerization barrier is related to π-bond energy.[29] In principle this is also true for partial double bonds. The latter type of rotation has been the subject of numerous investigations during the last decades by DNMR-spectroscopy.[3,7,30] The carbon–carbon double bond isomerization can be facilitated by steric hindrance of the ground state, which results in twisting or folding to some extent.[31–33] It is also facilitated by mesomeric stabilization by substituents at the double bond.[34] A review of all these effects is found in Ref 3.

Inversion is possible if one ligand at the double bond is represented by an electron or an electron pair. Examples of the general structure are the following:



HMO-calculations of the H_2ABH molecule have shown that the occupation of the $2b_2$-7a′ orbital leads to the c_s ground state symmetry[35] (the vinyl cation therefore has planar c_{2v} structure). The stereomutation of such c_s-species may involve a transition state of c_{2v} symmetry (inversion) or of nonplanar c_s' symmetry (rotation).

Distinction between rotation and inversion

The observed process of *Z,E*-isomerization is always the process of lowest energy. Theoretical as well as experimental evidence of the mechanism has been obtained for some special examples. It remains the question if generalizations are applicable to other cases. In the following section we will focus the discussion on the best studied cases of a C=X-structure, the imines.

The barrier of inversion is mainly determined by the energy change of the nonbonding orbital from sp^n to p.[36]‡ This is true for pyramidal as well as for planar inversion.[7,37–40] The occupation of the nonbonding orbital by only one electron therefore leads to low inversion barriers. The double bond order (which is responsible for the energy of the rotation) on the other hand is to the first approximation not affected by the number of electrons in the n-orbital. It is obvious that radicals such as vinyl radicals[41] or iminoxy radicals[17] isomerize by inversion (high rotation barrier, low inversion barrier). Calculated inversion barriers of some selected compounds in kcal/mol are:

1 2

4·3 kcal/mol[41] 31 kcal/mol[41]

(calculated by MINDO)

3 4

≤ 28 kcal/mol[42] 28 kcal/mol[42]

(calculated by CNDO)

†Many studies of photochemical *Z,E*-isomerizations have been reported.[25–27] Singlet as well as triplet mechanisms and different kinds of excited states[28] (e.g. π, π^*; n, π^*) have been proposed for these cases.

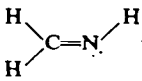
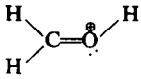
‡Non-empiric (*ab initio*) calculations have shown that the barrier of inversion is repulsiv dominant.[37–39]

Similiarly, one finds that the substituent effect of Z in vinyl radicals $H_2C{=}CZ^{43}$ is comparable to those found for inversion barriers of imines.

Many studies have been performed regarding the inversion mechanism of imines. The first discussion of the inversion mechanism was given by E. Hückel (1930).[15] In the middle of the 1960s it was again revived independently by Curtin *et al.*,[44] Staab *et al.*[45] and ourselves.[46] Meanwhile many arguments showed that the mechanism of *Z,E*-isomerization of imines proceed via an inversion or perhaps an intermediate mechanism which was inversional-like.[3]

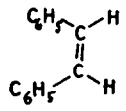
Calculations of methylenimine indicate that inversion is more favoured relative to rotation in this compound. The calculated barriers for rotation and inversion are collected in Table 1. The following *experimental* facts indicate an inversion-like mechanism for N-*aryl*-imines.

Table 1. Calculation of C_{2v} and C_s states for methyleneimine $H_2C{=}NH$ and protonated formaldehyde [in kcal/mol]

	Structure	Rotation C_s	Inversion C_{2v}	Ref
5		*ab initio* 57·5 CDNO/2 61·1	27·9 31·1	47 48
6		*ab initio* 31·4	17·2	49

1. *Double bond order and isomerizational barriers*

(a) Rotation about a C=N double bond should have a barrier comparable to or even higher than those of rotation about a corresponding C=C double bond. However, the experimental values are much smaller for imines than for the corresponding olefins.



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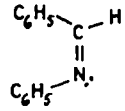
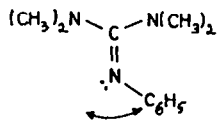
42·8 kcal/mol[50]



8

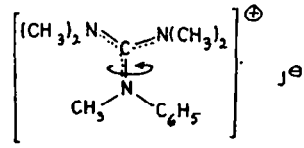
16·5 kcal/mol[51]

(b) The double bond order of guanidinium salts (< 33%) is much lower in comparison to the corresponding guanidines (~ 80% by CNDO/2 calculation.[52] If a rotation mechanism were operative one would expect a much higher barrier in the latter compounds. This is not the case.



9

12·1 kcal/mol[53]



10

11·1 kcal/mol[54]

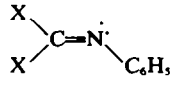
2. *Solvent effects*

(a) The *solvent polarity* does not influence the *Z,E*-topomerization barrier for guanidines, iminoesters and thiominoesters (Table 2).[55,57]

A polar transition state for rotation (as was observed for the *Z,E*-topomerization of polarized ethylenes) should lead to increasing rates with increasing solvent polarity.[34]

(b) *Protic solvents* (methanol) have a retarding influence on *Z,E*-topomerization rates (Table 2). This is explained by a hydrogen bond to the lone electron pair which is incorporated in the inversion mechanism. The same goes for the pyramidal inver-

Table 2. Free enthalpies of activation for *Z,E*-topomerization of some N-phenyl-imines in different solvents



Solvent	$\Delta G_c^{\ddagger}$[kcal/mol][a]			
	DK	**11** X = OCH_3[56,57]	**12** X = SCH_3[56,57]	**13** X = $N(CH_3)_2$[53,55]
CS_2	2·6	—	—	12·1
$CDCl_3$	4·7	14·3	13·6	11·9
CD_3COCD_3	20·7	14·2	13·65	12·0
CD_3CN	37·5	14·2	13·7	12·0
CD_3OD	34·0	14·7	—	12·9

[a] Free enthalpies of activation at coalescence temperature. Errors about 0·2 kcal/mol.

sion of nitrogen.[38] Protonation leads to immonium salts in which rotation occurs.[38,55]

(c) *Lewis acids*, such as $AlCl_3$, also render the *Z,E*-topomerization more difficult by complex formation with the lone electron pair.[59]

3. *Substituent effects in the aryl ring of N-aryl-imines*

(a) *Steric effect of* ortho-*substituents.* Bulky groups in *ortho*-position of N-aryl substituted imines facilitate the *Z,E*-isomerization (Fig 1). The *rotation* about the CN double bond should be hindered by large groups as it is observed for amides,[63,64] ketene aminals[22] and protonated as well as alkylated guanidinium salts.[54,55,58] The increasing steric strain destabilizes the angular ground state with respect to the linear transition state at inversion.

(b) *Electronic effect of* para-*substituents.* Hammett-correlations of *Z,E*-topomerization barriers have been found for substitution in para position in N-arylimines (Table 3). The ρ-value in all investigated cases except the N-aryl-hexafluoroacetonimines[69] are positive and of the same order. They are comparable to the ρ-value of the pyramidal nitrogen inversion of N-arylaziridines.[70]

A positive ρ-value can be taken as evidence against a biradical pathway or a polar rotational transition state involving a positive nitrogen.[60]

(c) *Stereochemical relations during isomerization.*

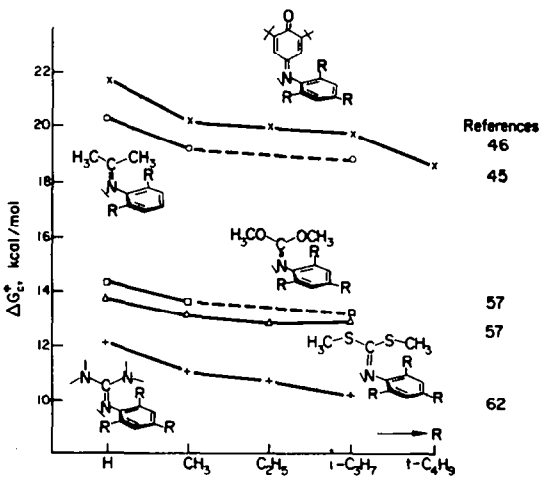


Fig 1. Steric effects on topomerization barriers of ortho-substituted N-aryl-imines.

Substitution of N-aryl imines with prochiral groups (e.g. isopropyl groups) in *o,o'*-position allows the simultaneous observation of *Z,E*-isomerization and enantiotopomerization.[14] If X = X', inversion (process **I⇌K** and **L⇌M**) as well as rotation about the N-aryl bond (process **I⇌L** and **K⇌M**) will change the prochirality of the substituent R, but C=N-double bond rotation (process **I⇌M** and **K⇌L**) will not.[71,72] The barriers for such compounds observed on R are the same as for **Z,E**-topomerization (ob-

Table 3. Influence of substitution on imino carbon and Hammett correlation of nitrogen inversion in N-aryl-compounds

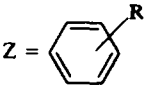
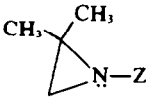
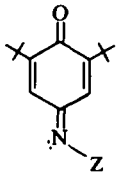
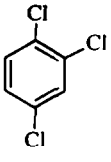
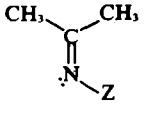
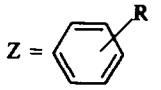
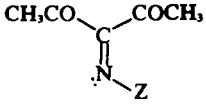
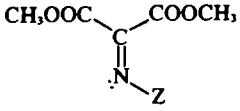
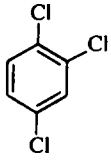
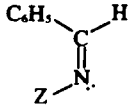
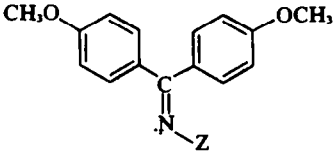
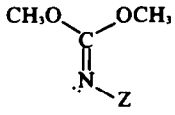
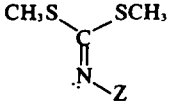
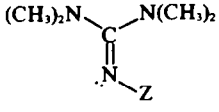
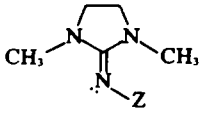
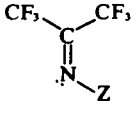
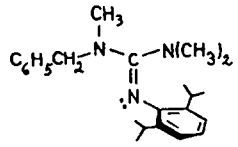
No.	Compound	Solvent	T_c [°C]	$\Delta G_c^{\ddagger}$ [kcal/mol]	T °C	ρ_T	ρ_{25}°	Ref
	Z = 							
14		CF_2Cl_2	−49	11·2	−60	2·8	2·0	70
15			140	22·2	100	1·5	1·9	60
16		C_6H_5—O—C_6H_5	126	20·3				45

Table 3—*Continued*

No.	Compound	Solvent	T_c [°C]	$\Delta G_c^{\ddagger}$ [kcal/mol]	T °C	ρ_T	ρ_{25}^{a}	Ref
	Z = 							
17		C_6H_5—O—C_6H_5	105	19·5				45
18			91	18·9				53, 62
19		C_2H_5OH C_6H_{12}			20 25	2·0 1·5	2·0[b] 1·5[b]	51 78
20		CCl_4	62	18·1	62	1·7	1·9	44
								
12		$(CD_3)_2CO$	−22	13·7	−25	1·6	1·3	56, 57, 67
13		$CDCl_3/CS_2$	−36	12·0	−50	2·95	2·2	53, 62
21		$CDCl_3/CS_2$	< −80	< 8				68
22		Pyridine	25	15·5	25	−1·0	−1·0	69

[a] For the sake of comparison the ρ-value for 25° was calculated.

[b] The influence of substitution in the phenyl-ring at the imino-carbon is very small. This has been used as an argument for the inversion mechanism.



E-27

served on the substituent X).* We can conclude that both observations belong to the same process (inversion). Therefore, the process I⇌K (L⇌M) is faster than I⇌M (K⇌L). If X≠X', again Z,E-isomerization is observed in the case of compound **27**. Of course the ground state enthalpy is different for both diastereomers (Table 4), but a small change of the structure gives only small differences to the corresponding guanidine of higher symmetry. The barrier of enantiotopomerization (observed when the magnetic nonequivalence of the *o,o'*-isopropyl groups disappears) is remarkably higher than those of *syn-anti* isomerization. These observations give evidence that at room temperature process I⇌K (L⇌M) is fast with respect to the NMR time scale, but it is not able to interconvert the structures **I** and **K** into **L** and **M** via N-aryl or C=N-double bond rotation (Fig 2). The latter process is much slower than inversion. The ratio of the rates of inversion k_{inv} and double bond rotation k_{rot} for this compound at room temperature is:

$$\frac{k_{Z,E}}{k_{enan}} = 10^{8.6} \Rightarrow \frac{k_{inv}}{k_{rot}} > 10^{8}.$$

*The smaller barrier for the enantiotopomerization process in the quinone anile indicates beginning N-aryl rotation. It is incompatible with fast CN-double bond rotation.

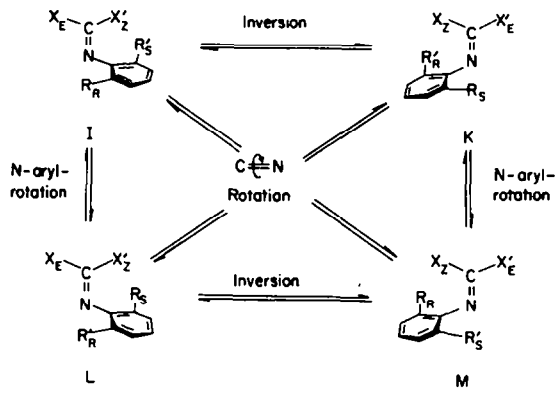
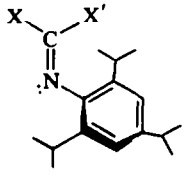


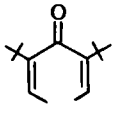
Fig 2. Intramolecular motions of N-arylimines.

It is obvious that a sychronous rotation about the C=N-double bond as well as N-aryl bond double rotation mechanism would lead to the same stereochemical consequence as pure inversion. The transition state **P** for such a double rotation mechanism is sterically strained by the interaction of the *ortho* substituent R with the imine system. Transition states of N-aryl-imines stereomutation Increasing the size of these substituents R, therefore, should cause an increasing isomerization barrier. This is in conflict with experimental results.

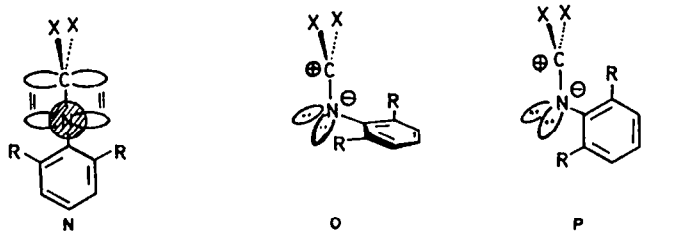
Although in our opinion these experimental data strongly support the inversion-like pathway for N-aryl imines, one cannot prove this mechanism for imines other than N-aryl imines with the same conclusiveness. On the other hand, the substituent effect on pyramidal nitrogen inversion and on imine stereomutation is very similar indicating a planar

Table 4. Topomerization and isomerization barriers of 2,4,6-triisopropyl-N-phenyl-imines

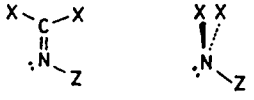


No.	X	X'	$\Delta G_c^{\ddagger}$[kcal/mol] Z,E-isomerization[a]	enantiotopomerization[b]
23			19·8	19·1
24	H_3CO	OCH_3	13·4	13·1
25	H_3CS	SCH_3	13·2	13·0
26	$(CH_3)_2N$	$N(CH_3)_2$	11·4	11·6
27	$(CH_3)_2N$	$N(CH_3)CH_2C_6H_5$	11·7[c]	23·5

[a] Coalescence of the X-signals; [b] coalescence of methyl signals of the isopropyl groups; [c] energy for interconversion of the more stabile *E* to the *Z* conformation. Energy differences between *E* and *Z*: $\Delta G° = 0·44$ kcal/mol.



inversion for the latter process. The rate of pyramidal inversion increases remarkably in the following sequence of substituents:

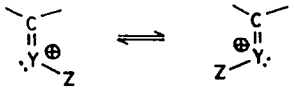


Z = alkoxy > dialkylamino > halogen > alkyl > aryl > acyl. As far as corresponding measurements on imines exist, the rates of stereomutation of these compounds follow the same order. It was possible to calculate pyramidal inversional by an empirical equation[73,74]

$$\Delta G_z^{\ddagger} = x \cdot z$$

where x represents a constant factor for the structure on nitrogen neglecting the substituent Z, while z depends only on the nature of the substituent of Z. It is interesting to note that to a first approximation the substituent constant z is the same for pyramidal inversion and planar inversion of nitrogen.[3,18] With this procedure it is possible to calculate inversion barriers. On the other hand, the discrepancies between such calculated barriers and the observed one can lead to the detection of other mechanisms (e.g. the catalysis of *Z,E*-topomerization of a hydrazone by tautomerization in certain solvents[18]).

Let us finally compare some other species isoelectronic to imines, e.g. ketonium salts and their sulfur analogs. The double bond order and therefore also the rotation barrier is generally lower in ketonium salts than in corresponding imines. The



Y = O,S

calculated barriers for rotation and inversion of protonated formaldehyde are shown in Table 1. Electron releasing groups lower the rotational barrier (e.g. protonated formic acid 14·3 kcal/mol for rotation, but 17·1 kcal/mol for inversion[49]). The rotation mechanism, therefore, is more probable in these compounds compared with the imines. There are several measurements of *Z,E*-isomerization barriers of protonated and alkylated carbonyl compounds which give *minimum* barriers of inversion *and* rotation, but give no evidence for mechanistic differentiation. The substituent effect of O-aryluronium salts supports a mechanism involving rotation about the partial C–O-double bond.

In contrast with the results of imines the isomerization barrier increases with increasing size of *ortho*-substituents. In Fig 3. these and similar results of thiouronium salts are shown. The barrier of the *o,o'*-ditert-butyl compounds represent the *minimum barrier* for planar inversion in these compounds. The inversion barrier for the corresponding nitrogen compound is not known, but one can conclude from the trend of effects that the barrier is much smaller ($\Delta G^{\ddagger} < 10$ kcal/mol[68]). The order of the barrier for planar inversion (O > N), therefore, is reversed from that of pyramidal inversion (N > O). A possible explanation of this fact is given

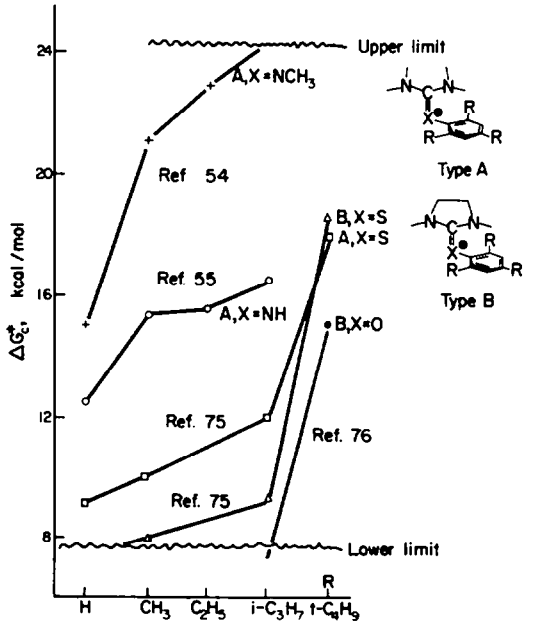
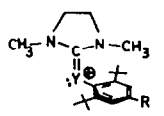
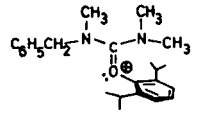


Fig 3. Steric effect of ortho-substituents on partial double bond rotation.





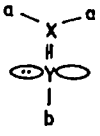
30

28: Y = O; R=CH_3 $\Delta G^{\ddagger}$ = 15·1 kcal/mol | $\Delta G^{\ddagger}_{z,E}$ < 10 kcal/mol

29: Y = S; R=C_4H_9 $\Delta G^{\ddagger}$ = 18·5 kcal/mol | $\Delta G^{\ddagger}_{enan}$ < 24·5 kcal/mol

below. It is not yet clear whether the observed magnetic nonequivalence of the ortho-isopropyl groups in **30** at 100° are due to a double rotation mechanism or to an inversion. The calculated optimum COH valence angle for the rotational transition state of protonated formic acid is 133° instead of 120° as in the ground state.[49] An increased valence angle also facilitates the double rotation. The larger the angle the closer the inversion transition state is approximated (optimal conjugation between the n-electron pair and the phenyl ring). An intermediate mechanism for uronium salts, therefore, seems to be possible.*

GS



TS

Substituent effect on planar inversion

The effects of structure variation on inversion barriers can be many-fold. Unfortunately the MO considerations and calculations which are done on special systems do not allow an interpretation of all influences of substituents.

1. *Population of the inverting orbital.* It is easy to see that the energy increases as more electrons have to be promoted from sp^2 to p (see p. 1862).

2. *Substituent b.* The influence of the substituent b on the planar inversion barrier is comparable to that of the pyramidal inversion. One may distinguish σ and π-effects. Electron attraction along the σ bond increases the s-character of the lone pair in the ground state increasing the inversion barrier. On the other hand, π-electron transfer from the inverting atom to p-type acceptor orbitals of the substituent b decreases the barrier by enhancing overlap in the transition state compared with the ground state. Reasonable explanations of these effects have been given perviously.[7,36-39]

3. *Inverting atom Y.* Pyramidal inversion barriers of the first row elements decrease in the order $C^{\ominus} > N > O^{\oplus}$.[38,77] With increasing positive charge of the nucleus, the separation between s and p orbitals and also inversion barriers decrease. In principle this should also hold for planar inversion, but there exists a second effect: the interaction of the inverting orbital with the two X–a bonds. This effect is also discussed in the stabilization of the transition state of rotation about the ethylenic double bond by hyperconjugation[28] and in the explanation of substituent effects of inversion in vinyl radicals.[43] The overlap between the p-type orbital at X increases on going from the ground state to the transition state.

This interaction of occupied orbitals is destabilizing† to the transition state of inversion (Fig 4). In going from Y = nitrogen to Y = oxygen the energy of the filled n-orbital is lowered in the transition state; the destabilization interaction increases.

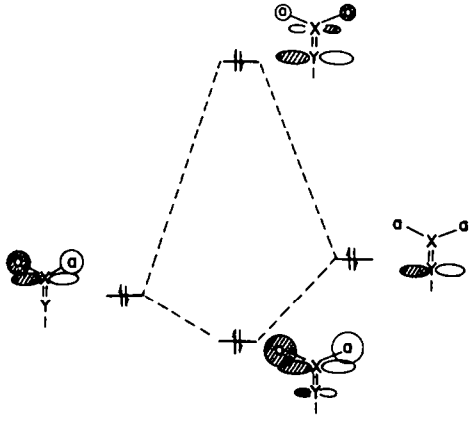


Fig 4. Interaction of occupied orbitals in the C_{2v}-state.

The above mentioned order of pyramidal inversion barriers is obviously overcome by this effect. Two competitive effects, therefore, influence the planar inversion states and calculations have to be performed to get insights into the relative importance of each of them.

4. *Substituents a.* It has been shown that substituents a lower the inversion barrier in the order:

$$\text{alkyl} > \text{aryl} > \text{RO} > \text{R}_2\text{N}$$

For explanation of this order we can again distinguish between σ and π-effects. Electron attraction in the σ bond lowers the energy of the orbitals at X. The destabilizing interaction of the X–a bonds with occupied p-orbital in the transition state is

*In our previous communication we have discussed the inversion mechanism for uronium salts.

†Besides this destabilizing interaction between the occupied p-type orbital at Y and the occupied π-type orbital of the Xa_2-group there is a second interaction between the occupied orbital at Y and the antibonding unoccupied highlying orbital at X; this second interaction, however, is small due to the large energy gap between the two interacting orbitals—as compared to the destabilizing one.

diminished—the barrier decrease. π-Conjugation obviously works in opposite direction. The latter effect is not yet proved by calculations.

5. *Nature of X.* To our knowledge there do not exist a systematic study of the role of X on inversion barrier of Y. The comparison of azobenzene ($E_a = 23$ kcal/mol) and benzalaniline ($E_a = 16$ kcal/mol) show decreasing barrier in the order X = C—N, but we will avoid further generalizations.

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