ASYMMETRICAL NONBRIDGEHEAD NITROGEN—30†
GEMINAL SYSTEMS—21‡

THE INFLUENCE OF VICINAL $n - \sigma^*$ INTERACTION ON THE PYRAMIDAL STABILITY OF TRICOORDINATED NITROGEN ATOM IN THE X̃-Ñ-Ỹ GEMINAL SYSTEM

G. V. Shustov,* A. B. Zolotoi and R. G. Kostyanovsky

Institute of Chemical Physics, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

Abstract—The vicinal $n - \sigma^*$ interaction stabilizes the pyramidal state of the nitrogen geminal system X̃-Ñ-Ỹ, where X and Y are electronegative substituents with high-lying levels of nonbonding n orbitals. A approximate value for the energy of $n - \sigma^*$ stabilization of pyramidal state in N,N-dialkoxyamines, equal to ~ 5.7 kcal/mol, has been found by comparing the average experimental value of the inversion barrier for these compounds with the one calculated according to the additive scheme. The influence of the vicinal $n - \sigma^*$ interaction on the structural peculiarities of N-alkoxyisoxazolidines manifests itself in the conformations with the greatest overlapping of n and σ^* orbitals being predominantly populated and in a change in N-O bond lengths and valence angles. The combination of a ligand having the highest-lying level of n orbital with a ligand, which forms the σ bond with a N atom, having the lowest-lying antibonding level results in the dissociation of a nitrogen geminal system into an ionic planar form of the X = N Y⁻ type. From this is inferred the dual nature of the influence exerted by the vicinal $n - \sigma^*$ interaction upon the inversion barrier of the X̃-Ñ-Ỹ geminal system.

The vicinal $n - \sigma^*$-interaction, as a factor influencing the inversion barrier of a N atom, was previously examined in the carbon geminal system X–C–N (where X = OH, OR) with the help of Hückel's simple method[3] and in the nitrogen geminal system X–N–Y (as exemplified by hydrazine, X = H, Y = NH₂, calculation *ab initio*[4a]) within the framework of the perturbational molecular orbital (PMO) theory.§

The interaction of a lone pair (LP) of the inverting atom with the antibonding orbital of the C–X bond lowers the inversion barrier by means of stabilizing the planar transition state,[3] as the energy of the nonbonding n-orbital rises[4,5] and increases $n - \sigma^*$ overlapping.[5c]


Scheme 1.
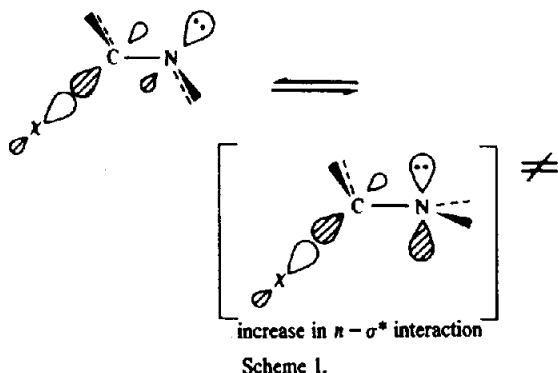
For nitrogen geminal systems, the relative acceptor capacity of the σ-bond in the planar and pyramidal states is of great importance. As the atomic population of the N atom[4b] and the overlap population of the bonds[4c,d] is greater in the transition state of inversion than in the ground state, the σ-bond of the N atom with an elec-

tronegative ligand will perhaps be the best internal acceptor in the case of a pyramidal molecule in comparison with a planar one. It follows that the vicinal $n - \sigma^*$ interaction must stabilize the pyramidal state to a greater extent.

Scheme 2.
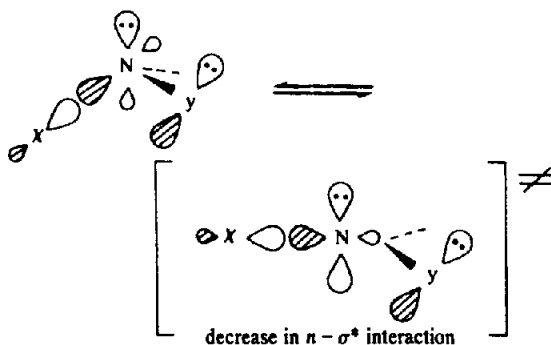
Hyperconjugation energy in geminal systems increases rapidly with increasing electronegativity of the ligand X (or Y) resulting from a decrease in the level and the localization of the antibonding orbital on the central atom.[6] Therefore, one can assume that, with the introduction to the N atom of two substituents, X and Y, of greater electronegativity than that of H and C and with high-lying levels of nonbonding orbitals (ṄR₂, ŌR, :F̈, :C̈l), besides the usual effect of heteroatoms (see reviews[7]), the vicinal $n - \sigma^*$ interaction will exert a substantial influence on the pyramidal stability of the N atom.

Scheme 3.

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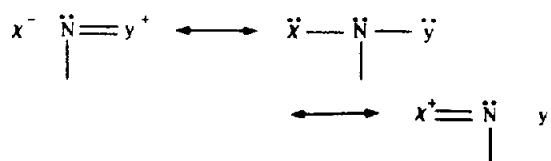
†Communication 29, see Ref. 1.
‡Communication 20, see Ref. 2.
§Pyramidal stability of AX₃ molecules, as a consequence of geminal $n - \sigma^*$ interaction, is examined from the standpoint of PMO theory.[5]

In the present work we shall try, on the basis of experimental data to estimate the energy of the vicinal $n - \sigma^*$ interaction in nitrogen geminal systems, to show its influence on the structural peculiarities of these systems and to reveal the dual nature of its effect on the pyramidal stability of N atom.
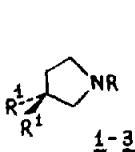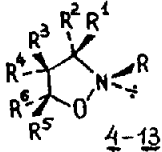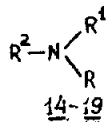
For nitrogen geminal systems the structure and configurational stability have been most studied for the case of N-alkoxyisoxazolidines and their acyclic analogues (Tables 1 and 2). The topomerization of these compounds, however, has its own specific features.

With the help of the NMR method[8] and X-ray studies (Table 2) it has been established that both in solution and in the crystalline state the invertomers of N-alkoxy-isoxazolidines exist only as anomers with a pseudoaxial position of the exocyclic MeO group. Therefore, inversion of the N atom is accompanied by conversion of the ring, the energy barrier of the latter being determined by the rotation around the N–O *endo* bond. As in the case of conventional alkyl-substituted hydroxylamines,[9] the inversion of the N atom in a cyclic N, N-dialkoxy-amines seems to proceed simultaneously with the rotation around at least one of the N–O bonds. The same is true for N-alkoxyisoxazolidines with respect to the N–O *exo* bond, whereas the overall transition state for inversion and rotation around the N–O *endo* bond for these compounds is substantially destabilized.[9] One can, therefore, assume successive transformation by way of rotation-inversion (Scheme 4) with a higher barrier for the latter process.
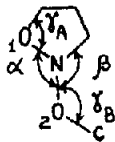
In the case of the pseudoequatorial isomer, where the O *endo* atom acts as the n-donor in $n - \sigma^*$, stabilization of the pyramidal state, is less effective (the ρ_A dihedral angle, Fig. 1, Table 2, increases to 60–70°), and this kind of stabilization is mainly actualized by the O *exo* atom. It is thus seen that in the general case $n - \sigma^*$ hypercon-

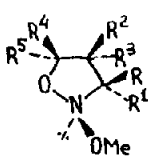Table 1. Configurational stability of pyrrolidines, isoxazolidines and their acyclic analogues

Compound	Solvent	$G^{\neq}$ a) kcal mol	Lit.
1 R=CD$_3$, R^1=Me	CHFCl$_2$	7.1	10a
2 R=Me, R^1=H	CHFCl$_2$	7.7	10a
3 R=OH, R^1=Me	CDCl$_3$	13.0	10a
4 R=Me, R^1=R^2=R^3=R^4=R^5=R^6=H	CDCl$_3$	15.6	10a
5 R=OMe, R^1=R^2=CO$_2$Me, R^3=R^4=R^6=H, R^5=CN	CDCl$_3$	28.5 b)	10b
6 R=OMe, R^1=R^2=CO$_2$Me, R^3=R^4=R^5=H, R^6=CN	CDCl$_3$	27.4	10b
7 R=OMe, R^1=R^5=CN, R^2=R^3=R^4=R^6=H	toluene	25.6	10c
8 R=OMe, R^2=R^6=CN, R^1=R^3=R^4=R^5=H	toluene	26.1	10c
9 R=OMe, R^1=CO$_2$Me, R^2=R^4=R^5=H, R^3=R^6=CN	toluene	27.9	10d
10 R=OMe, R^1=R^3=R^6=H, R^2=CO$_2$Me, R^4=R^5=CN	toluene	29.2	10d
11 R=OMe, R^1=R^4=R^5=CO$_2$Me, R^2=R^3=R^6=H	toluene	29.7	10d
12 R=OMe, R^1=R^4=R^5=H, R^2=R^3=R^6=CO$_2$Me	toluene	29.5	10d
13 R=OMe, R^1=R^2=CO$_2$Me, R^3=R^4=R^5=R^6=H	CHCl$_3$	27.5	10e
14 R=Me, R^1=R^2=CH$_2$Ph	CH$_2$=CHCl	6.2 b)	10f
		CH$_2$=CHCl	5.7	10g
15 R=OMe, R^1=Me, R^2=CH$_2$Ph	CH$_2$Cl$_2$	12.2 b)	10h
16 R=OH, R^1=R^2=CH$_2$Ph	CDCl$_3$	12.7	10i
17 R=OMe, R^1=Me, R^2=CMe$_2$CH$_2$CO$_2$Me	toluene	12.7	10j
18 R=OMe, R^1=OEt, R^2=CMe$_2$CH$_2$CO$_2$Me	toluene	24.6 b)	10j
19 R=OMe, R^1=OEt, R^2=CMe$_2$CO$_2$Me	toluene	23.6	10j

[a] $\Delta G^{\neq}$ values obtained at different temperatures[1,10] have been recalculated for 20° from formula $\Delta G^{\neq}_{T_1} = \Delta G^{\neq}_{T} + R(T - T_1)$ assuming that $\Delta S^{\neq}$ is close to 0,[7a] where this value is not indicated.
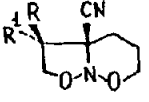
[b] To estimate the contribution of $n - \sigma^*$ hyperconjugation energy the following average values of experimental barriers have been taken: for 4–13 $\Delta G^{\neq}$ (NOR) = 27.9, for 14 $\Delta G^{\neq}_{R_2N}$ = 6.0, for 15–17 $\Delta G^{\neq}_{R_2NOR}$ = 12.5, for 18–19 $\Delta G^{\neq}_{RN(OR)_2}$ = 24.1 kcal/mol.

Table 2. Selected structural parameters and dihedral angles between the axes of n and σ^* orbitals in isoxazolidines and tetrahydro-1,2-oxazine
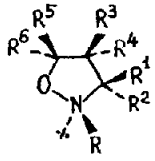

6   $R=R^1=CO_2Me$, $R^2=R^3=R^4=H$, $R^5=CN$

20 $R=R^1=CO_2Me$, $R^2=R^3=H$, $R^4=CN$, $R^5=Me$

21 $R=R^2=R^3=R^4=H$, $R^1=CN$, $R^5=Br\text{-}\langle O\rangle\text{-}$

22 $R=R^1=R^4=R^5=CONH_2$, $R^2=R^3=H$

23 $R=CO_2^-H_3\overset{+}{N}CH(Me)Ph(S)$, $R^1=CONHMe$, $R^2=R^3=R^4=R^5=H$
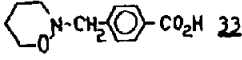
24 $R=OMe$, $R^1=LP$, $R^2=H$, $R^3=CO_2Me$

25 $R=OMe$, $R^1=LP$, $R^2=CO_2Me$, $R^3=H$

26 $R=LP$, $R^1=OMe$, $R^2=H$, $R^3=CO_2Me$

27 $R=H$, $R^1=Br\text{-}\langle O\rangle\text{-}$

28 $R=Br\text{-}\langle O\rangle\text{-}$, $R^1=H$

29 $R=Ph$, $R^1=R^2=Me$, $R^3=R^4=R^6=H$, $R^5=N(OH)Ph$

30 $R=Ph$, $R^1=R^2=Me$, $R^3=R^4=R^6=H$, $R^5=N(OH)Ph$

31 $R=Ph$, $R^1=H$, $R^2=Ph$, $R^3=CONEt_2$, $R^4=CF_3$, $R^5=R^6=F$

32 $R=Me$, $R^1=R^2=R^3=R^6=CO_2Me$, $R^4=R^5=H$

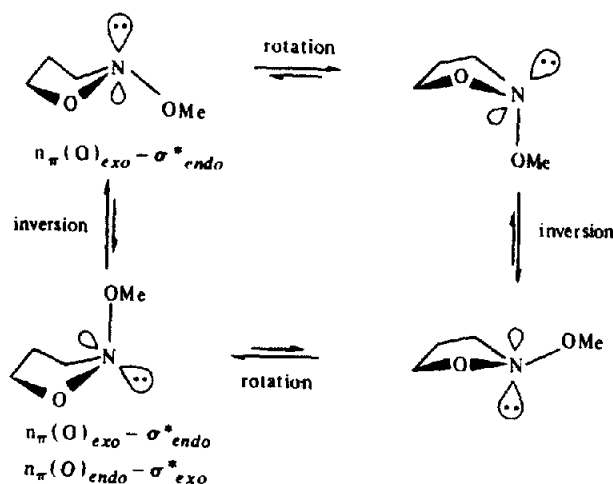33 (structure) $\langle \text{piperidine} \rangle N\text{-}CH_2\text{-}\langle O\rangle\text{-}CO_2H$

Compound	Bond length (Å) d_{N-O_1} / d_{N-O_2}	δd [a]	Valence angles (deg.) α / β	γ_A / γ_B	$\delta\gamma$ [b]	Dihedral angles (deg.) η_A / η_B	θ_A / θ_B	ρ_A / ρ_B	ω_A / ω_B	Lit.
6	1.43	0.01	108	–	–	42.3	65.5	24.5	78.4	11a,b
	1.44		100	–		164.1	88.4	1.6	52.2	
20	1.419	0.018	106.8	–	–	34.7	73.1	16.9	70.8	11b
	1.437		102.4	–		160.3	92.2	2.2	56.0	
21	1.412(8)	0.043	107.5(5)	109.1(5)	2.7	38.2	67.6	22.4	75.3	11c
	1.455(7)		101.0(5)	106.4(6)		172.0	81.4	8.6	44.7	
22	1.430(2)	0.005	107.4(1)	109.2(1)	1.2	33.9	73.9	16.1	70.0	10e
	1.435(2)		103.1(1)	108.0(1)		157.5	95.8	5.8	59.1	
23	1.418(3)	0.016	107.2(2)	109.5(2)	1.9	30.1	79.4	10.0	65.4	11d
	1.434(3)		104.5(2)	107.6(2)		163.2	87.6	2.4	52.2	
24	1.426(12)	0.014	106.0(8)	107.7(8)	1.1	40.2	66.3	23.7	76.9	11e
	1.440(12)		101.8(8)	106.6(8)		157.3	95.1	5.1	59.9	
25	1.420(6)	0.039	106.8(5)	109.1(4)	2.2	39.6	67.7	22.3	74.8	11f
	1.459(6)		102.9(5)	106.9(6)		149.5	104.7	14.7	67.6	
26	1.458(12)	-0.032	108.3(7)	112.9(7)	5.2	16.4	91.6	1.6	52.4	11e
	1.426(12)		103.5(8)	107.7(7)		169.9	84.8	5.2	47.6	

Table 2. (Contd)

Compound	Bond length (Å) d_{N-O_1} / d_{N-O_2}	δd a)	Valence angles (deg.) α / β	γ_A / γ_B	$\delta\gamma$ b)	η_A / η_B	θ_A / θ_B	ρ_A / ρ_B	ω_A / ω_B	Lit.
27	1.40 (2)	0.11	101 (1)	112 (1)	6	21.7	84.6	5.4	58.5	11g
	1.51 (2)		103 (1)	106 (1)		75.3	178.1	88.1	38.6	
28	1.41 (2)	0.03	103 (1)	108(1)	0	43.4	67.2	22.8	78.1	11g
	1.44 (2)		107(1)	108(1)		72.6	181.0	89.0	36.8	
29 c)	1.470(9)	–	–	104.2(6)	–	–	–	–	–	11h
	1.425(9) d)			–						
30	1.460(11)	–	–	103.2(7)	–	–	–	–	–	11h
	1.448(11) d)			–						
31	1.484(3)	–	–	108.2(5)	–	–	–	–	–	11i
32	1.466(3)	–	–	104.4(2)	–	–	–	–	–	1
33	1.456(6)	–	–	109.1(3)	–	–	–	–	–	11j

a) $\delta d = d_{N-O_2} - d_{N-O_1}$; b) $\delta\gamma = \gamma_A - \gamma_B$; c) 29 and 30 – two crystalline modifications; d) bond length of the N–O substituent of N(Ph)–OH.

$n_\pi(O)_{exo} - \sigma^*_{endo}$

inversion

rotation

OMe

OMe

$n_\pi(O)_{exo} - \sigma^*_{endo}$
$n_\pi(O)_{endo} - \sigma^*_{exo}$

inversion

rotation

Scheme 4.

jugation, decreasing the energy of the ground state of N, N-dialkoxyamines will increase the topomerization barrier, and, therefore, to be more precise one should speak of the influence of the vicinal $n - \sigma^*$ interaction on the configurational stability of N, N-dialkoxyamines.

This influence can be approximately estimated by comparing the experimental value of the topomerization barrier with the one calculated in accordance with the additive scheme, which presupposes that every ligand independently influences the configurational stability, raising it by its electronegativity and the destabilizing interaction of nonbonding orbitals in the transition state.

For N-alkoxyisoxazolidines, taking into account the different contributions of the exo and the endocyclic O atom from the data in Table 1, the topomerization barrier will amount to:

$$\Delta G^{\neq}\,(\text{NOR}) = \Delta G^{\neq}\,(\text{NMe}) + \Delta^{exo} + \Delta^{endo}$$

$$= 21.5 \ \text{kcal/mol}$$

where

$$\Delta^{exo} = \Delta G^{\neq}\,(\text{NOH}) - \Delta G^{\neq}\,(\text{NCD}_3)$$
$$= 5.9 \ \text{kcal/mol}$$

$$\Delta^{endo} = \Delta G^{\neq}\,(\text{O NMe}) - \Delta G^{\neq}\,(\text{NMe})$$
$$= 7.9 \ \text{kcal/mol}$$

Scheme 5.

The calculated barrier value is lower than the average experimental value ($\Delta G^* $ 27.9 kcal/mol, Table 1) by ~ 6.4 kcal/mol, which corresponds to the gain in energy due to the ground state stabilization by $n - \sigma^*$ hyperconjugation. This interaction was not taken into account in calculating the inversion barrier of N-methoxyisoxazolidine by extended Hückel theory (EHT).[11b] The value obtained in this case coincides with the experimental value only when the valence angle $\alpha = 104.5°$,
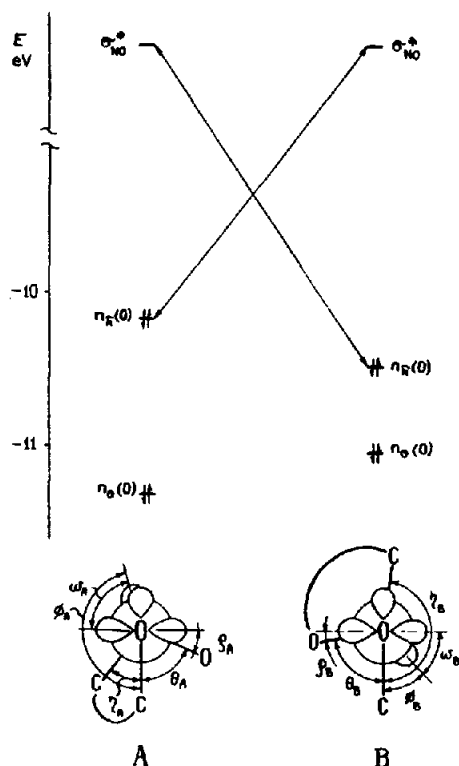
Fig. 1. Vicinal $n - \sigma^*$ interaction in N-methoxyisoxazolidines 6, 20-25. The energies of nonbonding $n_\pi(O)$ and $n_\sigma(O)$ orbitals for the O *endo* atom (fragment A, projection along O–N bond) and the O *exo* atom (fragment B) have been found from the $E(eV)$-$\beta(deg)$ relationship calculated by the MINDO/2 method for Me_2N–OMe.[13] For group $A < \beta$ is taken equal to $\sim 165°$, for B $\sim 45°$ (isoxazolidine 21). The LP of the central N atom, when N-methoxyisoxazolidine is arbitrarily divided into fragments A and B,[5c] falls on the secant plane and is not considered.

while the real α angle is 106–108° (Table 2). At this value of the angle the inversion barrier, $\Delta G^* \bigodot^{\text{Me}} \leqslant$ 22.7 kcal/mol, is close to that obtained using the additive scheme.[5]

However, the experimental ΔG^* values have been obtained for N-methoxyisoxazolidines 5–13 containing functional MeO_2C and CN substituents with low-lying antibonding π orbitals (Table 1) in the α-position with respect to the inverting N atom. Therefore, the gain energy $(\Delta G^*_{exp} - \Delta G^*_{calc})$ could also be attributed to $n - \pi^*$ interaction:[10b]
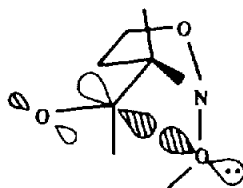
If this assumption is correct, the barrier for the transformation of the isomer with the *cis*-positioned donor (N–OMe) and acceptor (CO_2Me and CN) groups must always be higher than in the case of the *trans*-isomer. Actually, the inverse relationship is more often observed (see, e.g. ΔG^* for 7, 8 and 9, 10 in Table 1). But in those cases when the configurational stability of the *cis*-invertomer is higher than that of *trans*-invertomer the energy gain is only 0.2 kcal/mol (see ΔG^* for 11, 12 in

Table 1). An increase of the α angle by 8.0° in comparison with β in N-methoxyisoxazolidine 6 (Table 2) cannot be regarded as proof of an $n - \pi^*$ interaction either[10b,11a] since a similar difference in valence angles is also observed in isoxazolidine 21 with the donor and the acceptor groups in the *trans*-position, as well as in other isoxazolidines where $n - \pi^*$ overlapping is impossible for steric 24 or electronic 23 reasons (Table 2).

The topomerization barrier for acyclic N, N-dialkoxyamines on the assumption of the additivity of contributions made by OR groups, from the data in Table 1, will amount to:

$$\Delta G^*_{RN(OR)_2} = \Delta G^*_{R_3N} + 2\Delta^{OR} = 19.0 \text{ kcal/mol}$$

where

$$\Delta^{OR} = \Delta G^*_{R_2NOR} - \Delta G^*_{R_3N} = 6.5 \text{ kcal/mol}$$

Scheme 6.

The gain in energy $(\Delta G^*_{exp} - \Delta G^*_{calc}) = 5.1 \text{ kcal/mol}$ is somewhat smaller than that obtained for N-alkoxyisoxazolidines – 6.4 kcal/mol, but their average (5.7 kcal/mol) practically coincides with the value of bond separation energy[12] – 5.8 kcal/mol, calculated *ab initio* for dihydroxylamine HONHOH.[12b] In fact both these values reflect the contribution of $n - \sigma^*$ hyperconjugation to the stabilization of the ground state of the O–N–O geminal system.
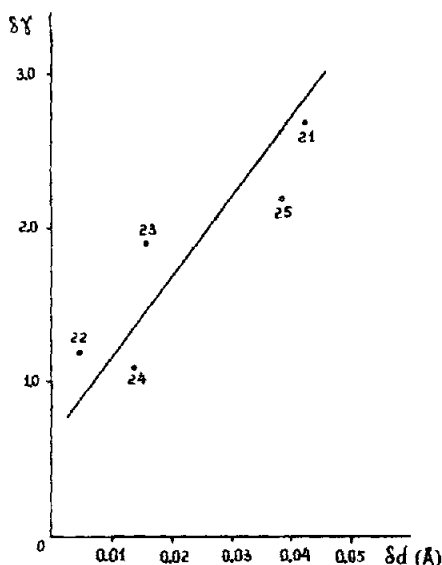
The vicinal $n - \sigma^*$ interaction influences the structural peculiarities of N-alkoxyisoxazolidines. For compounds 6, 20–25 with a conformationally mobile MeO *exo* group in the crystalline state, the populated conformation is the one with the maximum overlapping of $n_\pi(O)$ and σ^*_{NO} orbitals both of the N–O *endo* fragment (A) and the *exo* fragment (B) (Fig. 1). In this case the dihedral angles ρ_A and ρ_B between the axes of the interacting orbitals amount to 1.6–24.5° (Table 2). The close values of the torsion angles η and θ in the series of N-methoxy-isoxazolidines 6, 20–25 indicate that the dominant conformation is practically independent of the substituents in the isoxazolidine ring but is wholly determined by $n - \sigma^*$ overlapping. The preference of these conformations has also been obtained in EHT calculations without taking into account the hyperconjugation, based on the model of repulsion of localized electron pairs.[11b] However, as already shown for carbon geminal system both models, the "repulsive"[14] and the "attractive",[5c,6] despite their alternative nature, adequately explain the anomeric effect.

The shortening of the N–O *endo* bond in 6 and 20–25 by ~ 0.02 Å in comparison with the *exo* bond and by 0.05 Å in comparison with the N–O bond in N-phenyl- and N-methyl-substituted isoxazolidines 29–32 (Table 2) indicates that electron density is predominantly shifted to fragment B:

dominates
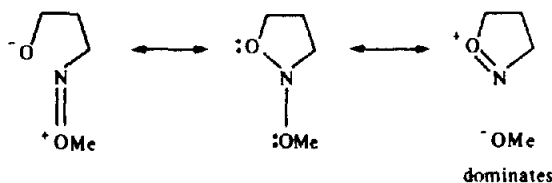
Scheme 7.

This also has a chemical consequence: the reaction of

Fig. 2. Correlative δγ–δ d dependence.

Fig. 3. Vicinal $n - \sigma^*$ interaction in 2,9-dioxa-1-azabicyclo(4.3.0)-nonanes 27 and 28. The energies of the nonbonding $n_\pi(O)$ and $n_\sigma(O)$ orbitals have been found, as in the case of 21 (Fig. 1), from[13] at $\beta_A \sim 148°$, $\beta_B \sim 51°$ (compound 27).

Scheme 8.

isoxazolidine 24 with BF_3 proceeds with the breaking of the longer N–O *exo* bond.[8c]

Moreover, an increase in the γ_A valence angle of the isoxazolidine ring, as compared to γ_B of the *exo* fragment (Table 2), also indicates a greater double-bond order of the N–O *endo* bond. We also found that the valence angle variation, $\delta\gamma$, correlates with bond length variation, δ d (Fig. 2); the shortening of the N–O *endo* bond in isoxazolidines 21–25 is, therefore, due to $n - \sigma^*$ interaction.

In one case only, for 26, the shortening of the N–O *exo* bond is observed despite the fact that γ_A is appreciably greater than γ_B and, similarly to other isoxazolidines, (6, 20–25) this compound exist in the crystalline state[11e] and in solution[8c,15] only in the form of a pseudoaxial anomer, whereas in carbon analogues the shortening of the C–O *exo* bond is characteristic for equatorial anomers.[16] It can, therefore, be assumed that the anomalous relation between the lengths of the N–O *exo*- and *endo* bonds in 26 is caused by the specificity of the sterically hindered steroid molecule.

The predominant shifting of electron density to the *exo* fragment B (Scheme 7) in isoxazolidines 6, 20–25 can be caused by the 4-electron $n_\pi(O)$–$n(N)$ interaction decreasing the level of the nonbonding π-orbital of the O atom with a decrease in dihedral angle ω between the LP axes[9,11b,13] (Fig. 1). Indeed, ω_B in the *exo* fragment B is smaller than the corresponding ω_A angle of the group fragment A in isoxazolidine. Hence, the $(E_{n_A} - E_{\sigma_B^*})$ energy difference must be smaller than $(E_{n_B} - E_{\sigma_A^*})$ and the stabilizing energy of n_A–σ_B^* interaction—greater than the n_B–σ_A^* energy.[5c]

Unlike the isoxazolidines 6, 20–25, in the bicyclic dialkoxyamines 27, 28 (Table 2), whose fragments are modelled by the isoxazolidine ring (A) with a pseudoaxial orientation of the N–O bond and the tetrahydro-1,2-oxazine ring (B) with an equatorial N–O *exo* bond (Fig. 3), the predominant shifting of electron density is only determined by the overlapping of $n_\pi(O)$ and σ^* orbitals. As follows from Fig. 3, the $n_\pi(O)_A$ and σ_B^* overlapping is maximal (ρ_A 5.4 and 22.8°) while $n_\pi(O)_B$ and σ_A^* are almost orthogonal (ρ_B 88.1 and 89.0°); the $n - \sigma^*$ hyperconjugation must, therefore, cause the shift of the charge to fragment B:
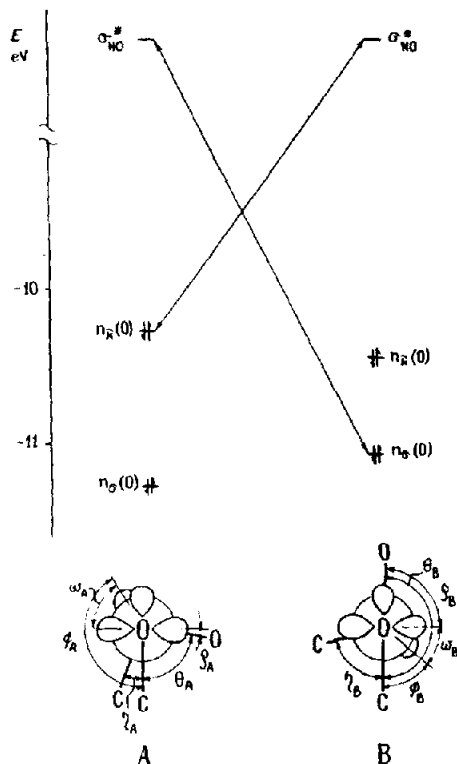
This is confirmed by the structural data and chemical properties: the N–O bond in the isoxazolidine rings 27 and 28 is shortened by 0.07 and 0.06 Å in comparison with conventional isoxazolidines 29–32, and the N–O bond in the tetrahydrooxazine ring 27 is elongated by ~ 0.05 Å as compared to tetrahydro-1,2-oxazine 33 (Table 2); rearrangements of this type in 2,9-dioxa-1-azabicyclo(4.3.0)-nonanes under the action of electrophilic reagents proceed with the breaking of only the N–O bond of the six-membered ring.[17]

The influence of the vicinal $n - \sigma^*$ interaction is also expressed by the broadening of the O–N–O (α) valence angle, as compared with O–N–C (β), in isoxazolidines 6, 20–26. Evidently, this interaction raises the population of antibonding orbitals of the N–O *endo* and *exo* bonds localized on the central N atom, which increases the repulsion between the N–O bonds.[18b] In the case of the unilateral $n - \sigma^*$ hyperconjugation in bicyclic dialkoxy-amines 27, 28, the antibonding orbital of the N–O bond is populated in the 6-membered ring only (scheme 8), and the repulsion between the N–O and the N–C bonds in this ring is greater than between the two N–O bonds. Hence, the β valence angle in the bicyclic rings 27, 28 is greater than α by $\sim 3°$ (Table 2). It is necessary to note that previously the X–A–X valence angle in the pyramidal AX_3 molecule was always observed to increase with

increasing electronegativity of the X ligands or decreasing electronegativity of the central atom A.[5,18] In this case, however, the systems investigated were those in which the vicinal interaction is either altogether absent (e.g. in CH_3^-, SiH_3^-, NH_3, PH_3) or is insignificant compared to the geminal interactions (e.g. in PF_3, NF_3).

The energy of the vicinal $n - \sigma^*$ interaction and, correspondingly, its contribution to the stabilization of the pyramidal state in the nitrogen geminal system X–N–Y will apparently increase when a ligand standing to the left in a row of the Periodic System of Elements (a better internal n-donor, e.g. R_2N^{5c} is combined with a ligand located more to the right within the row and in a lower column (a better internal σ-acceptor, e.g. Cl^{5c}). The bond separation energy† increases in the same order:[12c]

$$F-NH-F(5.6) < HO-NH-OH(5.8) < HO-NH-F(7.7)$$
$$= H_2N-NH-NH_2(7.7) <$$
$$< H_2N-NH-OH(10.7) < H_2N-NH-F(12.9).$$
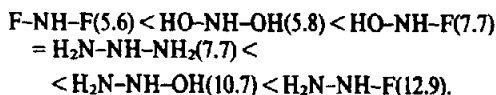
However, in selecting the substituents to obtain an X–N–Y geminal system with a high configurational stability it is necessary to bear in mind the following.

Firstly, a decrease in the LP ionization potential (increase in n-donating capacity) from right to left with a row and a decrease in the σ^* orbital level (increase in acceptor capacity) downwards in a column[5c] is accompanied by a decrease in the electronegativity of the elements:[19]

$$F(5.75) > O(5.21) > N(4.49) \quad F(5.75) > Cl(4.93)$$
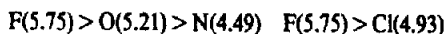
which will apparently compensate the energy gain obtained from n-$_{\sigma^*}$-hyperconjugation.

Secondly, a sharp narrowing of the $E_n - E_{\sigma^*}$ energy gap can result in the electron pair being transferred from the nonbonding to the antibonding orbital, which will cause the ionization of the N–X or N–Y bond, and the pyramidal $\ddot{X}$–$\ddot{N}$–$\ddot{Y}$ molecule will turn into a planar one, e.g. $X = \overset{+}{N} Y^-$. Indeed, this process takes place in the case of halogenation of hydrazines, when, instead, of $R_2\overset{+}{N}$–N(R)-Hal N-halogen hydrazines, the corresponding $R_2N = NR$ Hal$^-$ diazenium salts are observed or isolated.[20]

If a reaction is reversible as happens when the dynamic NMR method is used for the carbon geminal systems[21] (Scheme 9), an essentially different type of inversion, namely, dissociative inversion (Scheme 10) is possible. The latter, in distinction to the usual type, must proceed via an ionic intermediate following the pattern of S_N1 substitution.

$$R_2\ddot{N}-CH_2-F \rightleftharpoons R_2\overset{+}{N} = CH_2 + F^-$$

Scheme 9.

Scheme 10.

†Shown in brackets in kcal/mol.
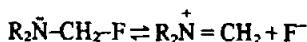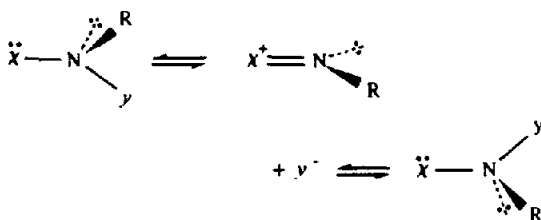
As yet unknown are the nitrogen analogues of fluoromethylamines-N-monofluorohydrazines,[22] and for other nitrogen geminal systems the equilibrium is shifted entirely towards either the covalent (RNF_2, $RNCl_2$, $RN(OR)_2$) or the ionic (diazenium salts) form. Nevertheless, it can be hoped that compounds with reversible dissociation of the N–Y or N–X bond will be obtained.

It is thus seen that the vicinal $n - \sigma^*$ interaction, as a factor influencing the configurational stability of $\ddot{X}$–$\ddot{N}$–$\ddot{Y}$ nitrogen geminal systems has a dual nature. In the general case this interaction stabilizes the pyramidal state. However, when a certain critical value is reached, which in the expression for the bond separation energy will be ~ 10 kcal/mol, it facilitates the transformation of a geminal system into an ionic planar form.

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