Configurational and Conformational Preferences in Oximes and Oxime Carbanions. Ab Initio Study of the Syn Effect in Reactions of Oxyimine Enolate Equivalents

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Abstract: Geometries and relative energies of stationary structures of several conformers of geometrical isomers of NO *s*-trans-configured acetaldoxime are reported. The calculated energies and geometries agree well with comparable experimental data. Effects of the theoretical model on the NO bond lengths are discussed for formaldoxime. (*E*)-Acetaldoxime prefers the conformation in which the in-plane CH_3 hydrogen and the CN double bond are cis; the staggered conformation is the transition-state structure for CH_3 rotation (E_a = 1.9 kcal mol^{-1}). In contrast, the rotation of the CH_3 group is virtually free in the Z isomer. (*Z*)- and (*E*)-acetaldoxime are almost isoenergetic, but their anions show a significant syn preference. Planar carbanions are minima, and all of the conformers with pyramidal CH_2 groups are transition-state structures for narcissistic rotation around the CC bond (E_a = 23.3–29.9 kcal mol^{-1}). At RHF/6-31+G*//RHF/3-21+G and at RHF/6-31+G*//RHF/6-31+G* the syn anion of acetaldoxime is preferred by 2.6 kcal mol^{-1} (2.0 kcal mol^{-1} including VZPEs), and CH_3/H substitution at the hetero-carbonyl C atom increases the syn preference energy to 7.3 kcal mol^{-1}. Electron density and analysis of the anions and the anti preference of the corresponding isomeric radicals (1.2 kcal mol^{-1} at PMP3/6-31G*//UHF/3-21G + VZPEs) show that 1,4-through-space conjugative stabilization of the syn anion is insignificant. Electrostatic effects appear to be more likely as the origin of the syn preference of the anions. Comparisons between the geometries of the free anions and those of the anions in the lithium and sodium ion pairs provide additional evidence for the ionic nature of the coordination of the metals. The theoretical results suggest that the regiochemistry of enolate equivalents of oxyimines in dissociating solvents is due to the thermodynamic syn preference of the anions. Syn/anti isomerization of the anions (E_a < 26 kcal mol^{-1}) is rapid even at low temperatures. In contrast, the anti preference of the radicals of acetaldoxime indicates that the formation of the syn products in oxidative coupling reactions of the anions of oxime ethers is a kinetic effect.

Metalated N-derivatives of carbonyl compounds have been employed with great success in stereoselective carbon–carbon bond-forming reactions.[2-4] Oxyimines such as oximes,[5-9] oxime ethers,[10-14] and oxazines[15] constitute an important class of substrates for such reactions. The reactions of metalated oxyimines with electrophiles show a high degree of regioselectivity; products of the syn-configured intermediate are generally obtained.[4-16] A high syn preference has also been found in oxidative coupling reactions of these enolate intermediates.[14]

Results are reported here off an ab initio study of configurational and conformational preferences of oximes and oxime carbanions to study the stereochemistry of these reactions.[17-19]

After a brief consideration of the structure of formaldoxime the relative stabilities of several conformations of the geometrical isomers of acetaldoxime are reported and compared to experimental data. Carbanions derived as conjugate bases of the oximes are taken to be suitable models for the study of enolate equivalents of oxime ethers. The structures of oximes (vide infra) and oxime ethers[20] are not sensitive to OR/OH substitution, and the electronic effects on the oxime skeleton and the change of the oxygen hybridization are expected to be small. The oximes are significantly smaller for ab initio computation.[21] In highly dissociating solvents the free ions are presumably the reactive species. Ion pairs[18,19,22] and aggregates[23] have been considered as reactive intermediates in solvents of low polarity. This ab initio study includes consideration of geometries, electronic structures, and origin of the thermodynamic syn preference, and the barriers to CC rotation and syn/anti isomerization of the carbanions of acetaldoxime. Relevant results also are discussed of the corresponding radicals. The geometries of the carbanions are compared to the neutral oximes and to the structures of the anions in lithium and sodium ion pairs.[18,19] The carbanions of acetketoxime and their ion pairs formed with lithium have been included to examine the effect of CH_3/H substitution at the hetero-carbonyl carbon atom.

Computational Aspects

Oximes can form a variety of stereoisomers. Hindered rotation around the NO bond gives rise to rotamers (*s*-cis and *s*-trans). Semiempirical[24] and ab initio[25,26] studies of formaldoxime have

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Table I. Comparison of Structures of Formaldoxime, $HONCH_2$ (1)[a]

	ab initio					
parameter	STO-3G[c]	3-21G[d]	4-31G[c]	3-21G*	6-31G*[d]	exptl[b]
HO	0.992	0.966	0.951	0.962	0.947	0.956
ON	1.409	1.446	1.420	1.377	1.369	1.408
NC	1.281	1.255	1.253	1.249	1.249	1.276
CH_s	1.087	1.072	1.071	1.081	1.078	1.085
CH_a	1.084	1.070	1.068	1.078	1.073	1.086
HON	101.4	103.8	106.1	102.8	104.5	102.7
ONC	110.7	111.2	111.4	111.8	112.0	110.2
NCH_s	123.8	122.7	122.6	122.7	122.6	121.8
NCH_a	118.2	117.9	117.5	117.5	117.3	115.9

[a] Bond lengths are in angstroms, angles are in degrees. H_s (H_a) and N are cis (trans) with respect to the CC bond. 3-21G* denotes a 3-21G basis set augmented by sets of six Cartesian d functions on all heavy centers with the 6-31G* d exponents of ref 33. [b] Reference 39. [c] Reference 37 and 26. [d] Compare ref 38.

Table II. Energies and Vibrational Zero-Point Energies[a]

	−energy[a]			
		6-31+G*//		
molecule[b] and sym	3-21+G	3-21+G	ZPE[c]	CSP[d]
1,[f] C_S $HONCH_2$	167.897 52	168.841 00		
2a, C_s (Z)-$HONCHCH_3$	206.725 24	207.879 34	48.83	M
2b, C_s	206.725 05	207.879 50	48.71	TS[e]
3a, C_s (E)-$HONCHCH_3$	206.724 69	207.880 60	48.59	M
3b, C_s	206.721 96	207.877 48	45.36	TS
4a,[g] C_s syn-X^-	206.150 69	207.257 41	38.91	M
4b, C_s syn-X^-	206.085 84	207.207 03	36.98	TS
4c, C_s syn-X^-	206.095 21	207.212 98	37.49	TS
5a,[g] C_s anti-X^-	206.148 19	207.253 28	38.27	M
5b, C_s anti-X^-	206.097 27	207.213 62	36.84	TS
5c, C_s anti-X^-	206.100 42	207.214 51	37.12	TS
6, C_1	206.114 29	207.214 68	37.66	TS
7, C_s syn-Y^-	244.972 05	246.294 28		
8, C_s anti-Y^-	244.962 94	246.282 69		
9, C_1 syn-Y^-Li^+	252.430 96	253.791 90		
10, C_1 anti-Y^-Li^+	252.415 98	353.786 63		

[a] Energies ($−E$) are given in atomic units and vibrational zero-point energies in kcal mol^{-1}. Molecules 1–3 were calculated without augmentation by diffuse functions; see text. No diffuse functions were used in the functional description of the CH_3 carbon atoms of 7–10. Lithium was described by a 3-21G or a 6-31G basis set, respectively. Local C_{3v} symmetry was imposed on tne methyl groups in 7–10; the frequency analysis of 7–10 therefore is prohibited. [b] $HONCHCH_2$ = X; $HONC(CH_3)CH_2$ = Y. [c] Unscaled. [d] Character of stationary point: M = minimum, TS = transition state (first-order saddle point), and SOSP = second-order saddle point. [e] See text. [f] Energies of 1 at other levels ($−E$ in au): E(3-21G*//3-21G) = 168.014 24; E(6-31G*//3-21G) = 168.836 98; E(3-21G*) = 168.017 67; E(6-31G*) = 168.841 00. [g] Energies ($−E$ in au) of 4a and 5a at RHF/6-31+G*//RHF/6-31+G* are 207.261 62 and 207.257 36, respectively.

shown the s-trans isomer to be favored by about 5–15 kcal mol^{-1}. We therefore consider all of the oximes and oxime carbanions only in their NO s-trans configurations. Instead, we focus on the geometrical isomers resulting from hindered CN rotation. The E/Z nomenclature is used for the oximes, and the syn/anti nomenclature is used to specify the position of the carbanionic center with regard to the HO group. In a syn anion, obtained by deprotonation of the CH_3 group of the (Z)-acetaldoxime, the CH_2 and the HO groups are cis with respect to the CN bond.

Single-determinant Hartree–Fock calculations were performed with the programs[27] GAUSSIAN80, GAUSSIAN82, and GAUSSIAN90. Restricted Hartree–Fock theory (RHF) was used for the closed-shell systems, and unrestricted HF theory (UHF) for radicals. Stationary structures were determined by gradient optimization[28] under the constraints of the symmetry point group using the 3-21G[29] and 3-21+G[30,31] basis sets, respectively, for the neutral molecules and the anions, respectively. Harmonic vibrational frequencies were calculated analytically to characterize stationary structures as minima or saddle points and to obtain vibrational zero-point energies. The vibrational zero-point energy corrections to relative energies were scaled (factor 0.9) to account for their usual overestimation at this computational level.[32] Energies were also calculated with these geometries and with the 6-31G* and 6-31+G* basis sets,[31,33] respectively. The UHF wave

functions are not eigenfunctions of the $\langle S^2 \rangle$ operator, and structures and energies therefore include contaminations from higher spin states.[34] Annihilation of the next highest spin states often removes the largest part of the spin contamination of the energies and, for this purpose, spin-projected unrestricted Hartree–Fock (PUHF) and second- and third-order Møller–Plesset (PMP2, PMP3) energies[35] were determined. The electrostatic properties of the carbanions were evaluated with the program MEPHISTO.[36]

Results and Discussion

Structures and Energies of Oximes. Formaldoxime. The parent oxime, formaldoxime, 1, has been considered in its planar s-trans conformation. Several semiempirical[24] and ab initio calculations[25,26,37,38] of 1 have been reported previously. In Table I optimized structures of 1 obtained at several basis set levels are summarized together with the experimental values (microwave r_s structure) reported by Levine.[39] Large differences are found for the NO bond length. The 3-21G basis set gives a NO bond length of 1.4 Å, indicative of a single bond.[40] Addition of polarization functions to the 3-21G basis set (3-21G*) and optimization at 6-31G* result in significantly shorter NO bonds. Geometry optimizations with polarized basis sets underestimate the bond length, whereas the use of unpolarized split-valence basis sets yields NO bonds that are too long by about the same magnitude. Similar discrepancies have been found for the related compounds acetamidoxime and hydroxylamine.[38] The recent calculations by Venanzi and Venanzi of the energy profile of

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Table III. Stationary Structures of Acetaldoxime[a-d]

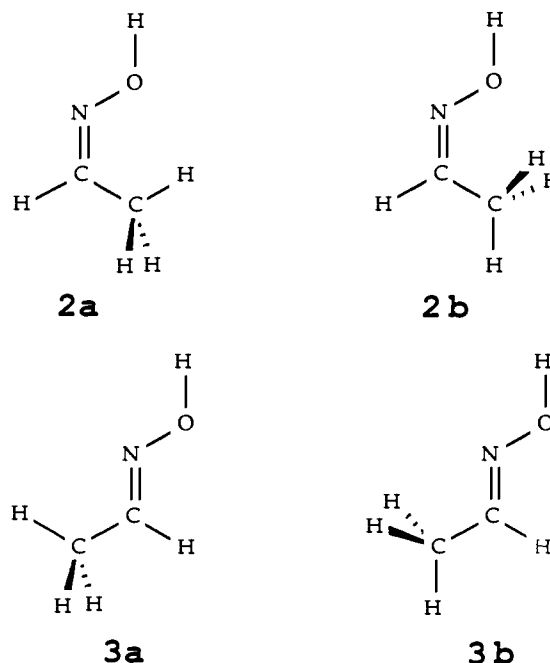|	Z isomer		E isomer	
parameter	2a	2b	3a	3b
H–O	0.966	0.966	0.966	0.966
O–N	1.450	1.451	1.451	1.452
N–C	1.258	1.259	1.256	1.256
C–C	1.501	1.502	1.502	1.510
C–H'	1.077	1.080	1.081	1.081
C–H''	1.085	1.083	1.085	1.083
C–H	1.074	1.073	1.075	1.074
H–O–N	103.2	103.5	103.6	103.5
O–N–C	111.7	110.3	109.9	109.9
N–C–C	128.1	126.1	120.7	120.5
H'–C–C	110.8	110.8	110.2	110.3
H''–C–C	109.7	110.0	110.2	110.6
H–C–N	114.4	114.9	110.2	120.3
H'–C–C–N	0.0	180.0	0.0	180.0
H''–C–C–H'	120.3	121.2	120.5	120.2

[a] At RHF/3-21G. In angstroms and degrees. [b] H' and H'' are the in-plane and out-of-plane methyl hydrogens, respectively. [c] Structure 3a has recently been published; see ref 41. [d] Compare ref 52.

(*E*)-acetaldoxime as a function of the CNOH dihedral angle undoubtedly also suffer from these deficiencies.[41] The accurate reproduction of experimental values for bond lengths that are affected by adjacent lone-pair interactions is a general problem in ab initio theory[42] since the gradients of the energy with regard to such bonds are rather small. Thus, little energy is required for moderate changes of the NO bond length. Bertolasi et al.[43] analyzed crystallographic data of a large number of oximes, and they found a strikingly large range (1.36–1.44 Å) for the NO bond lengths. Note that the mean value of 1.41 Å of these NO bond lengths equals that for 1 in the gas phase.[39] No intercorrelation between the NO and CN distances was found,[43] and the spread of the NO bond lengths can therefore not be attributed to differences in the importance of polar and nonpolar resonance contributions. The split-valence basis set calculations of 1 support this conclusion: The decrease of the NO bond length is accompanied by a decrease in the CN bond length as well.

All other structural parameters are far less basis-set dependent, and they are in good agreement with the structures of oximes determined by microwave spectroscopy[39] and neutron[38,44] or X-ray[45-51] diffraction studies. An interesting structural feature of 1 relates to the tilt of the methylene group. This feature is usually described by the tilt angle, that is, the angle enclosed between the CN axis and the line bisects the methylene group. The CH_2 group in 1 is bent toward the N lone pair with a tilt angle of 3.1°, and diffraction studies[45-49] suggest that this phenomenon is common for oximes. The ab initio calculations reproduce the structural feature.

Acetaldoxime. For both the (*Z*)- and the (*E*)-acetaldoximes, 2 and 3 respectively, two C_s symmetric conformations have been examined; see Scheme I. Calculated energies are summarized in Table II, and their optimized internal coordinates are listed in Table III. Bach and Wolber[52,53] have shown that the inter-

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Scheme I

2a   2b

3a   3b

conversion of the *Z/E* isomers of oximes requires about 60 kcal mol^{-1}.[54] The equilibration of the geometrical isomers of neutral oximes has more than twice the barrier for syn/anti isomerization of the carbanions (vide infra). Interconversion of the neutral *Z/E* oximes should therefore not play a determining role in the configuration of the enolate equivalents and is therefore not considered further in this study.

The ONC angles of 3a and 3b are 109.9° and close to the average angle of 111.1° found for the isomeric acetaldoximes. Gilli et al.[55] noted that the ONC angles of oximes are confined to a narrow interval (111–114°). The geometrical isomers differ to a significant extent only in their tilt angles. The HCN angle in 2 is increased compared to 1 and results in a larger tilt angle (6.8° in 2a and 5.6° in 2b), whereas the tilt angles in the *E* structures are essentially nil. These changes are presumably the consequence of minimization of repulsive (steric) interactions,

The calculated bond lengths of 2 and 3, respectively, are virtually identical and close to those in 1. All bond lengths agree well with comparable experimental data.[44-46] It had been proposed[44] that in similar bonding situations the CC bond length of the *E* isomer is that of a normal $C_{sp^2} - C_{sp^3}$ single bond, whereas the corresponding bond in the *Z* isomer is appreciably shortened, Our results, X-ray crystallographic data,[46-48] and ab initio results of related compounds[56] show both CC bonds to be of almost equal length.

Structures 2a and 2b of (*Z*)-acetaldoxime are nearly isoenergetic, and an essentially free rotation of the methyl group is indicated. At the RHF/6-31G*//RHF/3-21G level 2a is favored by only 0.10 kcal mol^{-1}; inclusion of vibrational zero-point energy corrections increases this energy difference to 0.21 kcal mol^{-1}. It is noteworthy that the 3-21G calculations indicate 2b to be slightly more stable than 2a and that the frequencies indicate 2b to be the transition-state structure for rotation of the CH_3 group. These results would indicate that 2b is the transition-state structure between a pair of enantiomeric minima that are more stable than

(54) The planar structure reported in ref 53 as the transition-state structure for N-inversion was not characterized by calculation of the Hessian matrix. Thus, the transition state may be nonplanar and the barrier might be lower. For example, narcissistic interconversion of NO s-*trans*-formaldoxime almost certainly involves a chiral transition-state structure in which the OH hydrogen is out of the plane of the molecular skeleton. Nevertheless, any resulting change in barrier height is probably relatively small.
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Table IV. Stationary Structures of Acetaldoxime Carbanions[a,b]

	syn isomer				anti isomer				
	4a		**4b**	**4c**	**5a**		**5b**	**5c**	**6[c]**
parameter	A	B	B	B	A	B	B	B	B
H–O	0.943	0.964	0.966	0.965	0.944	0.964	0.965	0.965	0.966
O–N	1.441	1.530	1.480	1.491	1.459	1.551	1.522	1.524	1.580
N–C	1.312	1.338	1.278	1.281	1.312	1.340	1.274	1.275	1.443
C–*C*	1.379	1.365	1.491	1.498	1.381	1.370	1.495	1.506	1.331
C–H$_s$	1.074	1.071		1.095	1.078	1.076		1.093	1.077
C–H$_a$	1.078	1.077	1.097		1.077	1.075	1.095		1.079
C–H	1.085	1.083	1.096	1.085	1.086	1.080	1.089	1.081	1.090
H–O–N	101.8	101.3	101.0	101.7	101.6	101.5	102.4	102.5	102.9
O–N–*C*	108.9	107.3	115.0	112.5	107.1	104.5	108.5	109.1	102.3
N–*C*–C	133.8	133.7	133.2	133.7	128.4	127.1	122.3	124.4	126.5
H$_s$–*C*–C	122.2	121.5		108.8	122.1	122.0		110.2	121.0
H$_a$–*C*–C	119.3	119.8	109.0		119.7	120.0	109.4		121.8
H–C–N	109.6	108.9	106.1	107.9	115.5	115.5	114.7	115.9	116.5
H$_s$–*C*–C–N	0.0	0.0		58.0	0.0	0.0		60.2	-2.9
H$_a$–*C*–C–N	180.0	180.0	120.9		180.0	180.0	120.4		178.1

[a] The deprotonated carbon atom is italicized. H$_s$ and H$_a$ are the hydrogens at the deprotonated carbon; H$_s$ (H$_a$) is oriented toward (away from) nitrogen. [b] A = RHF/6-31+G*; B = RHF/3-21G. [c] Further dihedral angles are O–N–C1–C2 = 81.5, H–O–N–C = -113.7, H–C–N–C = 176.3°.

the local minimum **2a**. At the 6-31G* level all of the vibrational frequencies of **2a** and **2b** are real and indicate these C_s structures to be minima.[57] The (imaginary) frequencies of the normal modes that promote the conformational change of **2b** are rather small (<50 cm⁻¹) at all levels. Correlation effects might also be crucial to the character of these structures, and a definite conclusion can thus not be made as to whether the methyl rotation involves two C_s minima and a pair of enantiomeric transition states or a C_s minimum, a pair of enantiomeric minima, a C_s transition structure, and a pair of enantiomeric transition structures. In any case, the effect of optimization at the 6-31G* level on the relative energies is negligible,[57] and the RHF/6-31G*//RHF/3-21G energies therefore appear to be satisfactory. The structure **3a** is the only minimum of the E isomer of acetaldoxime, and **3b** is the transition structure (204.2i cm⁻¹) for rotation of the methyl group. The activation barrier is 1.87 kcal mol⁻¹ (RHF/6-31G*//RHF/3-21G energies and VZPE(3-21G)).

Dorigo et al. have recently discussed the conformational preferences of molecules in which a methyl group is attached to a double bond.[58] The ground states of propene, acetaldehyde, and acetaldimines all show a preference of the order of 1–2 kcal mol⁻¹ for the conformation in which the in-plane methyl hydrogen and the double bond are cis. In agreement with these systems, we find **3a** to be more stable than the staggered (transition) structure **3b**, but our results show no such conformational preference for the (Z)-acetaldoxime; **2a** and **2b** are virtually isoenergetic, and there is barely any barrier to methyl rotation. It might be argued that steric repulsion between the in-plane CH₃ hydrogen and oxygen in **2a** or additional stabilization of **2b** as a result of two electrostatically favorable interactions between the CH₃ hydrogens and oxygen compared to one such interaction in **2a** may be responsible for the small conformational preferences in **2**, but any interpretation of this sort bears little physical significance since the differences are small and too many factors probably contribute to it.

The average energies of the conformations of the geometrical isomers **2** and **3** of acetaldoxime show a syn preference of 0.24 kcal mol⁻¹ at RHF/6-31G*//RHF/3-21G. This syn preference vanishes when zero-point energy corrections are included. The calculated energies are in reasonable agreement with experimental Z/E ratios of acetaldoxime of 64:36[59] and 61:39[60] as measured by ¹³C NMR and ¹H NMR spectroscopy, respectively.[61]
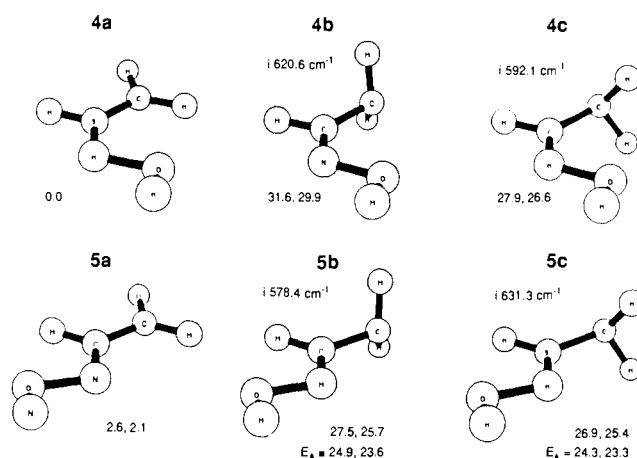

Figure 1. Stationary structures of acetaldoxime carbanion. The isomeric planar anions **4a** and **5a** are minima. All other structures are transition-state structures for CH₂ rotation. Relative energies and activation barriers for rotation of the CH₂ group are given as calculated at RHF/6-31+G*//RHF/3-21+G without and with inclusion of vibrational zero-point energy corrections calculated at RHF/3-21+G.

Oxime Carbanions: Models for Anions of Oxyimines. Six C_s symmetric (**4a–c** and **5a–c**) and one asymmetric (**6**) stationary structures (Table IV) have been located for the carbanions derived from acetaldoxime. In the structures **4a–c** the deprotonated carbon atom and the hydroxy group in a syn relation with each other; **5a–c** are the corresponding anti isomers. The planar delocalized anions **4a** and **5a** are minima; all other structures are transition-state structures for rotation around the CC bond (**4b**, **4c**, **5b**, and **5c**) or for syn/anti isomerization (**6**). For acetketoxime the π-conjugated syn- (**7**) and anti-configured (**8**) carbanions have been considered (Table V). A cisoid orientation of the in-plane hydrogen of the methyl group and nitrogen was assumed for **7** and **8**. A conformational change of the methyl group should affect the energies but little (vide supra). Energies and vibrational zero-point energies are listed in Tables II.

Structures and Syn-Preference Energies. The three occupied a″ orbitals are the π-MOs of acetaldoxime; deprotonation of the α-carbon of acetaldoxime moves the nodes of MOs 2a″ (one extra node) and 3a″ (two extra nodes) from the CC bonding region into the NO (MO 2a″) and the CN (HOMO 3a″) regions. Accordingly, the CC bond shortens (by 0.13–0.14 Å) and increases of about equal magnitude (0.08–0.10 Å) result for the CN and

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(58) Dorigo, A. E.; Pratt, D. W.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 6591.
(59) Hawkes, G. E.; Herwig, K.; Roberts, J. D. *J. Org. Chem.* **1974**, *39*, 1017.
(60) Karabatos, G. J.; Taller, R. A. *Tetrahedron* **1968**, *24*, 3347.

(61) For further references and NMR spectroscopic studies of chromatographically separated syn and anti isomers of oximes, see: Wimmer, Z.; Saman, D.; Smolikova, J.; Romanuk, M. *Liebigs Ann. Chem.* **1988**, 1091.

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Table V. Structures of Isomeric Carbanions from Acetketoximes **7** (*C_s*, syn) and **8** (*C_s*, anti) and Their Lithium Ion Pairs **9** (*C_1*, syn) and **10** (*C_1*, anti)[a,b]

	syn isomer		anti isomer	
	Y⁻	Li⁺Y⁻	Y⁻	Li⁺Y⁻
parameter	**7**	**9**	**8**	**10**
H–O	0.964	0.962	0.963	0.967
O–N	1.526	1.563	1.547	1.477
N–C	1.341	1.382	1.346	1.352
C–*C*	1.366	1.358	1.377	1.386
C–H_s	1.070	1.072	1.075	1.081
C–H_a	1.078	1.073	1.076	1.071
C–E	1.530	1.517	1.530	1.510
H–O–N	101.1	106.1	99.8	104.8
O–N–C	107.9	105.7	109.5	111.6
N–C–*C*	131.0	127.9	121.4	116.8
N–C–E	109.9	109.9	121.4	121.2
C–*C*–H_s	121.2	121.5	121.5	119.5
C–*C*–H_a	120.0	119.6	120.2	120.1
H_s–*C*–C–N	0.0	−18.4	0.0	−30.3
H_a–*C*–C–N	180.0	175.6	180.0	173.9
E–C–N–*C*	180.0	173.9	180.0	173.2
O–N–C–*C*	0.0	6.3	180.0	182.1
H–O–N–C	180.0	136.5	180.0	229.9

[a] The deprotonated carbon atom is italized. H_s and H_a are the hydrogens at the deprotonated carbon; H_s (H_a) and N are cisolid (transoid). E = CH₃. [b] HONC(CH₃)CH₂⁻ = Y⁻. [c] Local *C*₃ᵥ symmetry was imposed on the methyl groups. The structural parameters are in **7** (**9**) CH = 1.084 (1.083) Å, HCC = 110.1° (110.1°), and they are in **8** (**10**) CH = 1.081 (1.082) Å, HCC = 109.9° (110.1°).

Table VI. Structures and Energies of the Syn- and Anti-Configured Radicals HONCHCH₂•, **4r** and **5r**[a]

	structures[a,b]				
parameter	**4r**	**5r**	parameter	**4r**	**5r**
HO	0.966	0.967	HON	104.1	104.5
ON	1.436	1.437	ONC	109.2	107.1
NC	1.355	1.357	NCC	126.8	120.0
C*C*	1.374	1.473	HsCC	120.8	120.7
*C*H_s	1.068	1.072	HaCC	120.2	120.7
*C*H_a	1.071	1.071	HCN	112.6	118.2
CH	1.072	1.072			

	energies[c]		
method[d,e]	**4r**	**5r**	SPE
UHF/3-21G	206.128 42	206.128 17	0.16
UHF/6-31G*	207.277 00	207.278 76	−1.10
UMP2/6-31G*	207.844 77	207.845 84	−0.67
PUHF/6-31G*	207.297 28	207.299 03	−1.10
PMP2/6-31G*	207.862 17	207.863 29	−0.70
PMP3/6-31G*	207.884 28	207.885 71	−0.90

[a] Minimum structures (*C_s*, NO *s*-trans, in angstroms and degrees) optimal at UHF/3-21G. The unscaled vibrational zero-point energies are 39.51 and 39.18 kcal mol⁻¹ for **4r** and **5r**, respectively. [b] The deprotonated carbon atom is italicized. H_s and H_a are the hydrogens of the CH₂ group; H_s (H_a) is oriented toward (away from) N. [c] Energies (−E in au) are based on the UHF/3-21G geometries. All MOs were used in the perturbation calculations. [d] ⟨S²⟩ values: syn radical 1.0006 (UHF/3-21G), 0.7600 (PUHF/3-21G), 0.9983 (UHF/6-31G*), 0.7598 (PUHF/6-31G*); anti radical 1.0043 (UHF/3-21G), 0.7604 (PUHF/3-21G), 1.0005 (UHF/6-31G*), 0.7602 (PUHF/6-31G*). [e] ⟨S²⟩₁ values of the 6-31G* wave functions are 0.9258 (syn) and 0.9282 (anti).

Figure 2. Structures of the planar NO *s*-trans-configured radicals **4r** (syn) and **5r** (anti).

the NO bonds. The changes in bond angles are such as to reduce electrostatic repulsion between the CH₂ carbon and oxygen (in **4a**) or nitrogen (in **5a**), respectively, by increasing the tilt angles (e.g., from 6.8° in **2** to 12.4° in **4a** and from essentially zero in **3** to about 5.8° in **5a**). Methyl/H substitution has remarkably little effect on the bond lengths of the anions; they vary by no more than 0.01 Å (Tables IV and V). The angle changes are larger for the anti anions than for the syn anions. In *syn*-**7** the CH₃ group causes the NCE angle (E = CH₃) to increase by only 1.1°, and the NCC and CNO angles increase but slightly (1.7° and 0.6°, respectively) compared to **4a** (E = H). The title angle found for *syn*-**4a** is maintained in its homologue. More significant increases of the NCE and the CNO angles (5.9° and 5.0°, respectively), are found for **8** compared to **5a**. Concomitant with the increase of the NCE angle, the NCC angle is decreased by 5.7°. In short, these structural effects indicate that the anions are best simply regarded as vinylamide anions.

The syn-preference energy of 2.6 kcal mol⁻¹ calculated[18] at RHF/6-31+G*//RHF/3-21+G is reduced to 2.0 kcal mol⁻¹ when vibrational zero-point corrections are taken into account. The syn preference is larger for the carbanions of acetketoxime for which the syn-preference energy is 7.3 kcal mol⁻¹ at RHF/6-31+G*//RHF/3-21+G.
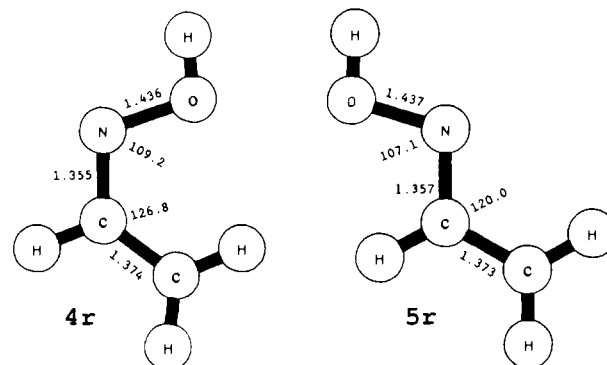
Geometry optimizations were also carried out at the RHF/6-31+G* level for the anions **4a** and **5a** (Table IV). Compared to the RHF/3-21+G structures, the NO bond lengths are greatly shortened (by about 0.09 Å), small increases of the CC bond lengths (0.01 Å) and decreases of the CN bond lengths (0.02 Å) occur, and the effects on bond angles are marginal. The basis-set effects on the anion geometries parallel those discussed above for formaldoxime; that is, it appears likely that the NO bond lengths determined at RHF/6-31+G* are too short while those optimized at RHF/3-21+G are too long. The RHF/6-31+G*//RHF/6-31+G* energies of **4a** and **5a** are lower by 2.64 and 2.56 kcal mol⁻¹, respectively, than the RHF/6-31+G*//RHF/3-21+G energies. The virtually complete cancellation of the basis-sets effects on the isomeric structures results in a syn-preference energy of 2.67 kcal mol⁻¹ at the RHF/6-31+G*//RHF/6-31+G* level, only 0.08 kcal mol⁻¹ higher than that obtained at RHF/6-31+-G*//RHF/3-21+G.

Origin of the Syn Preference of Oxime Carbanions. Most discussions have interpreted the syn preference as an intrinsic

property of the carbanion[62] caused by favorable orbital interactions in the syn isomer.[63,64] The arguments presented in the following provide evidence that such conjugative stabilization is insignificant.

The coefficients of the 3a″ MOs in the anions **4a**, **5a**, **7**, and **8** indicate that these anions are best described as three-center-four-electron π-systems that are only moderately perturbed by the oxygen π-density rather than as four-center-six-electron π-systems. The hydroxy O and the C(C) atom do have AO coefficients in the HOMOs that are of comparable magnitude and with the proper phase to allow for 1,4-through space conjugation in the syn anions; however, proper phase relationships need to be combined with sufficient overlap to provide effective cyclic conjugation, and such overlap is lacking. Note that deprotonation

(62) For discussions of related isomeric systems see: (a) Hartmann, J.; Muthukrisnan, R.; Schlosser, M. *Helv. Chim. Acta* **1974**, *57*, 2261. (b) Geiss, K.-H.; Seuring, B.; Pieter, R.; Seebach, D. *Angew. Chem.* **1974**, *86*, 484. (c) Seebach, D.; Enders, D. *Angew. Chem.* **1975**, *87*, 1. (d) Fraser, R. R.; Ng, L. K. *J. Am. Chem. Soc.* **1976**, *98*, 5895. (e) Evans, D. A.; Andrews, G. C.; Buckwalter, B. *J. Am. Chem. Soc.* **1974**, *96*, 5560. (f) Bates, R. B.; Beavers, W. A.; Greene, M. G.; Klein, J. H. *J. Am. Chem. Soc.* **1974**, *96*, 5640. (g) Fraser, R. R.; Grindley, T. B.; Passannanti, S. *Can. J. Chem.* **1975**, *53*, 2473.
(63) Hoffmann, R.; Olofson, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 943.
(64) (a) Epiotis, N. D.; Bjorkquist, D.; Bjorkquist, L.; Sarkanen, S. *J. Am. Chem. Soc.* **1973**, *95*, 7558. (b) Epiotis, N. D.; Sarkanen, S.; Bjorkquist, D.; Bjorkquist, L.; Yates, R. *J. Am. Chem. Soc.* **1974**, *96*, 4075.

of acetaldoxime, **2a**, to give **4a** is accompanied by an *increase* in the distance between the CH_2 carbon and the oxygen by 0.05 Å. The electron density projection function[65] of **4a** shows no significant amount of electron density between the hydroxy O and the CH_2 carbon.[19] Such 1,4-overlap could be identified in the contour map of the projection function by the presence of a projection bond path connecting the oxygen and the CH_2 group and a resulting projection ring critical point $(2,0)_p$.[66,67] Such features are not present in the projection function of the syn carbanion of acetaldoxime.[19] 1,4-Conjugation effects would also be expected to affect the minimum values of the electron density projection function along the bonds (MPD); they should be smaller in **4a** than they are in **5a**. The MPD values (in e au^{-2}) of **4a** (CC, 0.67; CN, 0.65; NO, 0.44) and **5a** (CC_1 0.67; CN, 0.65; NO, 0.42) indicate no such differences.

The relative stability of the radicals produced by homolytic cleavage of a methyl CH bond of **2** and **3** allows for a further test of the importance of homocyclic conjugation. Optimal geometries of the radicals were calculated by UHF theory at the 3-21G level, and these structures are probably reasonably reliable.[68] Structural parameters of the planar radicals **4r** (syn) and **5r** (anti) are listed in Table VI and molecular-model-type drawings are shown in Figure 2. The most significant structural difference between the radicals and the corresponding anions is the large decrease of the NCC angles; $\angle$(NCC) = 6.9° (syn) and 7.1° (anti). The NCC angles are reduced more than the ONC angles are increased (syn, 1.9°; anti, 2.6°) compared to the anions. The CH_2 carbon and the oxygen are 0.11 Å closer in the radical **4r** than in the anion **4a**. If homocyclic conjugation were the primary source of the syn preference of the carbanions, then *syn*-**4r** would be expected to be favored over *anti*-**5r**. The syn stabilization could be expected to be smaller than for the anion since the 3a″ MO is singly occupied, but, on the other hand, the structure of the radical allows for larger overlap. Various energies of **4r** and **5r** are summarized in Table VI. The eigenvalues of $\langle S^2 \rangle$ are 1.00 for both isomers at the UHF/6-31G*//UHF/3-21G level. Second-order Møller–Plesset perturbational corrections for electron correlation reduce the spin contamination but little[35,69] ($\langle S^2 \rangle_1$ = 0.93, see Table VI), but the annihilation of the quartet spin states effectively removes the largest part of the spin contaminations ($\langle S^2 \rangle_{PUHF}$ = 0.76) and the total energies are significantly lowered. The relative energies of the isomers are affected less. We found that *anti*-**5r** is favored over *syn*-**4r** by 1.1 kcal mol^{-1} at UHF/6-31G* and PUHF/6-31G*, and the perturbational corrections for electron correlation yield only slightly smaller anti preference energies of 0.7 (UMP2, PMP2) and 0.9 kcal mol^{-1} (PMP3). The inclusion of the (scaled) vibrational zero-point energies calculated at UHF/3-21G increases the anti preference by 0.3 kcal mol^{-1}, and our best estimate of the anti-preference energy is thus 1.2 kcal mol^{-1} (PMP3/6-31G*//UHF/3-21G + VZPE).

These results show that homoconjugative stabilization is unimportant. The thermodynamic syn preference of the anions is more likely the result of electrostatic effects. The electrostatic repulsion between the N_σ lone pair and the CH_2 carbon in the anti anion could be larger than the repulsion between the O lone pairs and the CH_2 carbon in the syn isomer. This argument is supported by the larger syn preference of the anions of acetketoxime compared to the anions of acetaldoxime. The ONCC skeletons of the syn configured carbanions **4a** and **7** differ but little, whereas the NCC angle in **8** is significantly smaller than in **5a**. It needs to be emphasized that any attempt to explain such small
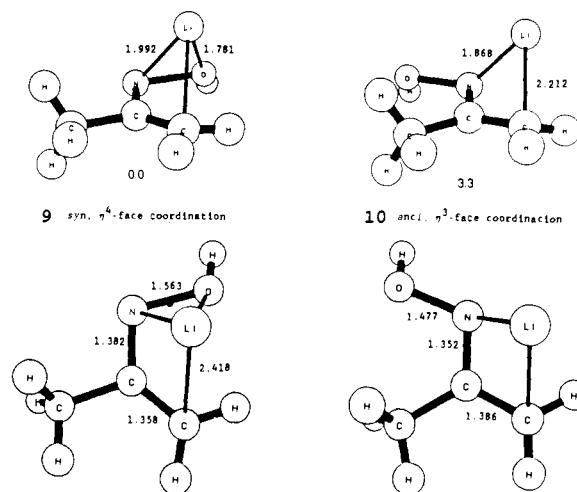

Figure 3. Structures of the lithium ion pairs of isomeric acetaldoxime carbanions. Lithium engages in η^4 face coordination in the syn-configured ion pair **9** and lithium bridges in a η^3 fashion in the anti-configured ion pair **10**.

energy differences between isomers lacks rigor since these differences are undoubtedly the result of a delicate balance of a manifold of interrelated geometric and electronic factors, and all of these factors are different in the isomers.

We have previously reported populations[65] of the anions **4a** and **5a**.[19] These populations show that most of the charge is localized on the heteroatoms and on nitrogen in particular.[66] The IPP values of the N atom and of the HO group are –0.78 (–0.75) and –0.35 (–0.38) in **4a** (**5a**), respectively.[19] The charges of the CH_2 groups are –0.42 (**4a**) and –0.46 (**5a**), and the CH groups are electron deficient. The charge distribution is simply described as the result of localization of the entire charge on the heteroatoms and polarization of the $CHCH_2$ fragment.[70] The high charge of the N atoms in the anions finds its manifestation in the geometries. The ONC angle of oximes is known to be confined to a small range (vide supra), and its change thus represents a sensitive probe for electronic reorganization. Deprotonation causes a decrease of the ONC angle by 4.5° and 5.4° for **4a** and **5a**, respectively. Deprotonation causes increased electron–electron repulsion and the π-MOs become larger; the contributions of the outer diffuse basis functions are more significant in the anions. This is true in particular for nitrogen because of its large charge. The σ-MOs become less shielded, and radial contraction of the electron density can offset some of the destabilization. Radial contraction is particularly stabilizing for an MO that describes a lone pair; a larger electron–nucleus attraction is achieved without concomitant reduction of bonding overlap. The significantly increased *s* character of the σ-MO 15a″ (mainly N_σ) is thus a direct consequence of the deprotonation. Because of the increased *s* character of the N_σ lone pair, the CN and NO bonds involve larger contributions from p-type N-AOs and the ONC angle decreases.

Effect of Ion Pair Formation on Anion Geometries. We reported recently some results of a theoretical study of the regiochemistry of the lithium and the sodium ion pairs of acetaldoxime that suggest that the syn-preference energy is increased upon formation of the ion pairs.[18,19] Since the syn preference of the acetketoxime anions exceeds that of the acetaldoxime anions substantially, one might expect that CH_3/H substitution at the heterocarbonyl C

(65) (a) Collins, J. B.; Streitwieser, A., Jr. *J. Comput. Chem.* **1980**, *1*, 81, and references therein. (b) McDowell, R. S.; Grier, D. L.; Streitwieser, A., Jr. *Comput. Chem.* **1985**, *9*, 165.

(66) For a comparison between integrated projection populations and populations defined by the theory of atoms in molecules (including data of the isomeric oxime carbanions of acetaldoxime), see: Glaser, R. *J. Comput. Chem.* **1988**, *10*, 118.

(67) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9, and references therein.

(68) For a comparison between UHF/3-21G structures with experimental data see ref 42, p 194.

(69) Gill, P. M. W.; Pople, J. A.; Radom, L.; Nobes, R. H. *J. Chem. Phys.* **1988**, *89*, 7307.

(70) This type of charge distribution is typical for such 1,2-dihetero four-center sixe-electron π-systems, and it is fundamentally different from the electronic structures of 1,3-dihetero four-center six-electron π-systems, such as the carbanions of methyl formate or *N*-methylformamide (Rondan, N. G.; Houk, K. N.; Beak, P.; Zajdel, W. J.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *20*, 4108). In the 1,2-systems the CH_2 group is attached to an electron-deficient C atom, but it is attached to an electron-rich heteroatoms in the 1,3-systems. Consequently, in the 1,2-systems the "carbanion" becomes stabilized by charge delocalization, but in the 1,3-systems the minimization of electron–electron repulsion leads to charge localization, CH_2 pyramidalization, and orthogonalization between the CH_2 lone pair and the one of the adjacent heteroatoms.
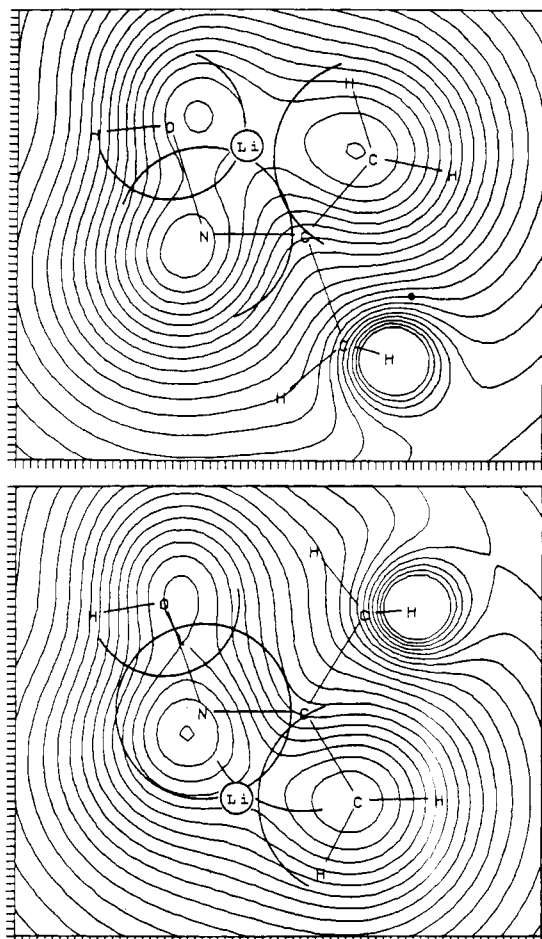
Figure 4. Contour maps of the purely Coulombic electrostatic potentials of the syn- (top) and the anti-configured carbanions of acetketoxime **7** and **8**, respectively. Contour levels start at −0.26 (syn) or −0.27 au (anti) with a level spacing of 0.01 au. The electrostatic potential in the plane parallel to and separated by 1.5 Å from the molecular plane is displayed. Arcs show normal Li–Y bond distances.

atom might also significantly affect the syn preference of the corresponding ion pairs. The lithium ion pairs formed with *syn*-**7** and *anti*-**8** acetketoxime carbanions were therefore optimized. The η^4 face coordinated syn ion pair, **9**, and the η^3 NC bridged anti ion pair, **10**, are shown in Figure 3, and structural parameters are listed in Table V. These modes of coordination are likely to be favored over η^2 NO bond coordination in metalated oxime ethers.[19] Bond distances involving Li^{+} are virtually identical with the values found for the ion pairs of acetaldoxime.[18,19] Ion pair formation reduces the syn preference compared to the free carbanions of acetketoxime, but the syn-preference energy of 3.31 kcal mol^{−1} (RHF/6-31+G*//RHF/3-21+G) is about the same as for the ion pairs of acetaldoxime.

By analysis of the electrostatic potentials of the isolated carbanions from acetaldoxime we have found that the position of the cation in the ion pairs agrees well with the position of maximal electrostatic attraction in the area determined by typical closest approach distances between lithium and the atoms of the anion.[18,19] The agreement is equally good for the purely Coulomb potential or with inclusion of polarization corrections. Polarization effects do change the magnitude of the electrostatic potential, but its topology is affected comparatively little.[71] This approach has now been applied to the analogous ketoxime system. Contour maps of the Coulomb potentials of **7** and **8** in planes parallel to the molecular plane and appropriate for containing the Li^{+} are shown in Figure 4. The agreement between the positions of the metals and the locations of maximal electrostatic interaction is

(71) Streitwieser, A., Jr.; Boussie, T.; Dixon, R.; Glaser, R.; Gronert, S.; Krom, J.; Wang, P. *J. Comput. Chem.*, to be submitted.

Table VII. Comparison of the Structures of the Syn-Configuration Carbanion of Acetaldoxime and Its Ion Pairs[a–c]

parameter	HX **2a**	X[−] **4a**	η^4 face Li^{+}X[−]	η^4 face Na^{+}X[−]	η^2 bond Li^{+}X[−]	η^2 bond Na^{+}X[−]
H–O	0.966	0.964	0.962	0.965	0.967	0.968
O–N	1.450	1.530	1.564	1.547	1.564	1.558
N–C	1.258	1.338	1.378	1.377	1.381	1.366
C–C	1.501	1.365	1.347	1.347	1.334	1.342
C–H_s	1.077	1.071	1.072	1.072	1.071	1.072
C–H_a	1.085	1.077	1.073	1.073	1.073	1.072
C–H	1.074	1.083	1.077	1.079	1.079	1.079
H–O–N	103.2	101.3	106.5	107.9	109.8	110.0
O–N–C	111.7	107.3	104.8	106.5	109.6	110.0
N–C–C	128.1	133.7	130.6	132.1	131.4	132.0
N–C–H	114.4	108.9	109.0	108.6	108.5	108.6
C–C–H_s	110.8	121.5	121.9	122.2	122.4	123.2
C–C–H_a	109.7	119.8	119.4	119.7	120.0	119.9
H_s–C–C–N	0.0	0.0	−16.8	−10.0	2.9	5.0
H_a–C–C–N	120.9	180.0	175.1	177.4	181.3	181.5
H–C–N–C	180.0	180.0	172.6	175.0	181.2	180.8
O–N–C–C	0.0	0.0	5.2	6.0	−2.0	2.2
H–O–N–C	180.0	180.0	135.1	103.4	73.4	35.8

[a] The η^4 face coordinated ion pairs of lithium and sodium are compounds **9a** and **14a**, respectively, and the η^2 NO bond coordinated isomers are structures **9b** and **14b**, respectively, in ref 19. [b] The deprotonated carbon atom is italicized. H_s and H_a are the hydrogens at the deprotonated carbon; H_s (H_a) is oriented toward (away from) N. [c] HONCHCH_2[−] = X[−].

Table VIII. Comparison of the Structures of the Anti-Configured Carbanion of Acetaldoxime and Its Ion Pairs[a–c]

parameter	HX **3a**	X[−] **5a**	η^3 face Li^{+}X[−]	η^3 face Na^{+}X[−]	η^2 bond Li^{+}X[−]	η^2 bond Na^{+}X[−]
H–O	0.966	0.964	0.967	0.966	0.966	0.966
O–N	1.451	1.551	1.481	1.485	1.582	1.586
N–C	1.256	1.340	1.349	1.360	1.397	1.387
C–C	1.502	1.370	1.374	1.363	1.332	1.336
C–H_s	1.081	1.076	1.081	1.081	1.074	1.074
C–H_a	1.085	1.075	1.071	1.072	1.073	1.073
C–H	1.075	1.080	1.077	1.078	1.076	1.079
H–O–N	103.6	101.5	105.2	105.6	109.1	109.9
O–N–C	109.9	104.5	109.4	107.8	106.6	106.8
N–C–C	120.7	127.1	120.7	123.2	123.8	124.1
N–C–H	120.6	115.5	117.8	116.6	115.5	109.9
C–C–H_s	110.2	122.0	120.4	121.8	122.0	121.5
C–C–H_a	110.2	120.0	120.1	120.7	120.3	120.6
H_s–C–C–N	0.0	0.0	−27.1	−23.8	−3.6	−5.4
H_a–C–C–N	120.5	180.0	173.6	171.0	176.3	173.8
H–C–N–C	180.0	180.0	171.9	175.9	178.3	176.9
O–N–C–C	180.0	180.0	184.6	162.9	171.9	164.3
H–O–N–C	180.0	180.0	233.1	247.1	−88.4	−48.9

[a] The η^3 face coordinated ion pairs of lithium and sodium are compounds **10a** and **15a**, respectively, and the η^2 NO bond coordinated isomers are structures **10b** and **15b**, respectively, in ref 19. [b] The deprotonated carbon atom is italicized. H_s and H_a are the hydrogens at the deprotonated carbon; H_s (H_a) is oriented toward (away from) N. [c] HONCHCH_2[−] = X[−].

comparable to the aldoxime case and provides a compelling argument for essentially ionic bonding.

The comparison of the geometries of the isolated anions with the geometries of the anions in the ion pairs provides further evidence for the dominantly ionic metal–ligand bonding in the ion pairs. Tables V, VII, and VIII show that ion pair formation affects the bond lengths of the anions but little. The NC bonds are slightly lengthened, and the CC bonds are moderately shortened on ion pair formation. Ion pair formation also reinforces the vinylamide ion character of the anions compared to the free ions. Any relaxation in the carbanions also provides a probe for the relative importance of the lithium contacts. The lithium position of the η^3 CN bridged lithium ion pair of acetaldoxime was optimized, keeping the geometry of the carbanion fixed to the geometry of **5a**; bond distances found between Li and the

Reactions of Oxyimine Enolate Equivalents

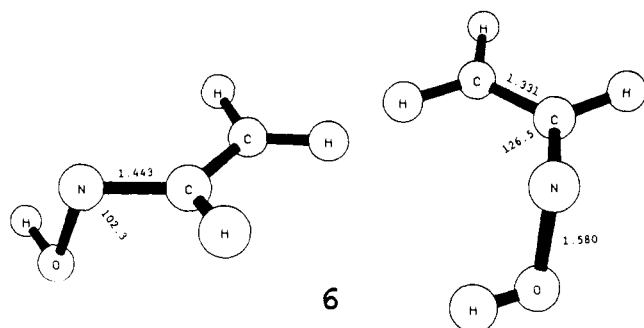*J. Am. Chem. Soc., Vol. 111, No. 19, 1989* 7347

Figure 5. Transition-state structure **6** for syn/anti isomerization of the acetaldoxime carbanions. Relative energies and activation barriers are given as calculated at RHF/6-31+G*//RHF/3-21+G without and with inclusion of vibrational zero-point energy corrections calculated at RHF/3-21+G.

atoms C(C), C(N), and N are 2.42, 2.17, and 1.90 Å, respectively.[72] The relaxation of the CH_2 group and the decrease of the NCC angle in the fully optimized structure[18] cause decreases in the LiC(C) distance (0.15 Å) and the LiN distance (0.03 Å). Optimization of the lithium derivative of the rigid anion **4a** results in bond distances between Li and O, N, and C(C) of 1.85, 2.05, and 2.38 Å, respectively. Full optimization of the structure[18] causes both of the LiO and LiN bond lengths to decrease by 0.07 Å, whereas the LiC distance is increased by 0.12 Å. These results suggest that the carbanion relaxation serves primarily to allow for electronic reorganization that causes a shift of electron density toward the heteroatoms in order to optimize the chelation of Li^+ by the heteroatom(s). The ONC angle, a sensitive probe for the charge of nitrogen (vide supra), supports this argument; this angle decreases on formation of the syn-configured ion pairs.

Narcissistic CH_2 Rotation in Acetaldoxime Carbanions. The transition-state structures **4b** and **4c**, and **5b** and **5c** (Figure 1) for CH_2 rotation in the syn and the anti anions, respectively, are localized carbanions with typical CN double and CC single bonds and pyramidal CH_2 groups (Table V). The anti-configured structures **5b** and **5c** are 25.7 and 25.4 kcal mol^{-1}, respectively, less stable than the planar minimum *anti*-**5a** at RHF/6-31+G*//RHF/3-21+G and including vibrational zero-point energies. **5b** and **5c** are essentially isoenergetic although it might have been expected that **5b** is destabilized from a repulsive interaction between the C_σ and the N_σ lone pairs. The syn-configured transition structures are less stable than the corresponding anti structures. The higher energy of **4c** compared to **5c** may result from steric interactions between the HO group and the CH_2 hydrogens and **4b** apparently suffers from repulsion between the C and O lone pairs.

The higher energies of **4b** and **4c** compared to **5b** and **5c** together with the syn preference of the planar structures result in significant differences in the activation barriers for CC rotation in the isomeric anions. The zero-point energy-corrected activation barriers for rotation of the CH_2 group in the anti anion via **5b** and **5c** are 23.6 and 23.3 kcal mol^{-1}, respectively, whereas the activation barriers are 29.9 and 26.6 kcal mol^{-1} for rotation in the syn anion via **4b** and **4c**, respectively.

Syn/Anti Isomerization of Acetaldoxime Carbanions. The stationary structure shown in Figure 5 has one imaginary frequency (317.6i cm^{-1}), and the transition vector identifies this structure, **6**, as the transition-state structure for syn/anti isomerization of the acetaldoxime carbanion. The interconversion between the isomeric carbanions is accomplished by rotation of the HO group around the CN axis. The change of the hybridization of nitrogen and the concomitant loss of the π-delocalization lengthen the CN bond and shorten the CC bond (Table IV)

compared to **4a** and **5a**. The orientation of the hydrogen of the HO group is such that the conformation of the HONC fragment (dihedral angle HONC = 113.7°) resembles the conformation of hydrogen peroxide ($HOOH_{expl}$ = 119.1°). The repulsion between the adjacent lone pairs remains substantial despite this favorable arrangement, and it is presumably responsible for the major part of the activation barrier. The zero-point energy corrected activation barriers for the processes **4a** → **6**‡ → **5a** and **5a** → **6**‡ → **4a** are 25.7 and 23.7 kcal mol^{-1}, respectively, at RHF/6-31+G*//RHF/3-21+G. The activation barriers for syn/anti isomerization and for rotation of the CH_2 group are of comparable magnitude although the electronic reorganizations associated with the processes differ greatly. Rotation of the CH_2 group requires a substantial shift of electron density from the heteroatoms to the CH_2 group along the reaction pathway to the carbanionic transition structures, whereas the charge distributions in **4a** and **5a** already exhibit much of the imide anion character of the transition structure **6**.

Summary and Conclusions

The ab initio calculations of the oximes yield structures and relative energies that are in good agreement with comparable experimental data. The NO bond length is rather susceptible to small changes in the theoretical model. (E)-Acetaldoxime shows a distinct preference (1.9 kcal mol^{-1}) for the conformation in which the in-plane CH_3 hydrogen and the CN double bond are cis; but, in contrast to other systems that contain the CH_3—CR=X skeleton, it is found that there is practically no barrier to methyl rotation in the Z isomer. The geometrical isomers of acetaldoxime are almost isoenergetic in good agreement with the small Z preference determined by NMR measurements. A significant thermodynamic isomer preference has been found for the carbanions of oximes. Planar carbanions, best described as vinyl-amides with little π-delocalization, are minima, and all of the conformers with pyramidal carbanionic CH_2 groups are transition-state structures for CH_2 rotation. At both of the levels RHF/6-31+G*//RHF/3-21+G and RHF/6-31+G*//RHF/6-31+G* the syn-configured carbanion of acetaldoxime is preferred over the anti isomer by 2.6 kcal mol^{-1} (2.0 kcal mol^{-1} with vibrational zero-point energy corrections). CH_3/H substitution increases the syn-preference energy to 7.3 kcal mol^{-1} for the carbanions of acetketoxime. Analysis of the electron density projection functions of the carbanions and the anti preference of the corresponding radicals (1.2 kcal mol^{-1} at PMP2/6-31G*// UHF/3-21G + VZPEs) provide strong evidence that 1,4-through-space conjugative stabilization of the syn anion is insignificant. Electrostatic effects seem more likely as the origin of the thermodynamic syn preference of the anions.

The large increase of the syn-preference energy of the anions of acetketoxime compared to the anions of acetaldoxime suggests that CH_3/H substitution might also significantly affect the isomer stabilities of the ion pairs. The comparison between the lithium ion pairs of acetketoxime and the previously reported ion pairs of acetaldoxime shows that the methyl substituent has but little effect on the ion pairs and does not much affect the syn preference of the ion pairs. The similarities between the structures of the free anions and the structures of the anions in the ion pairs as well as the evaluation of the electrostatic properties of the free anions provide additional evidence for the dominantly ionic nature of the metal coordination in these metalated enolate equivalents.

This theoretical study suggests that the regiochemistry of reactions of enolate equivalents of oxime ethers in dissociating solvents is due primarily to the thermodynamic stabilities of the isomeric anions. The calculated barrier to syn/anti isomerization of the anions (<26 kcal mol^{-1}) indicates that rapid equilibrium may occur even at low temperatures. A kinetic preference for the addition of an electrophile to either of the isomeric carbanions might also contribute to the overall regiospecificity, but there is no apparent reason why such kinetic effects should be significant. In contrast, the anti preference of the radicals of acetaldoxime points up that the formation of the syn products in oxidative coupling reactions of the anions of oxime ethers must be due to

(72) The energies (−E in au) of the partially optimized syn- (anti-) configured ion pair are 213.595 242 (213.578 737) and 214.750 985 (214.731 891) at RHF/3-21+G and RHF/6-31+G*//RHF/3-21G, respectively. The syn-configured ion pair is favored by 10.36 and 11.98 kcal/mol at RHF/3-21+G and RHF/6-31+G*//RHF/3-21+G, respectively.

kinetic control. The syn products result in these reactions because the syn/anti isomerization of the radicals formed by oxidation of the free anions (or by oxidation of the anions in the ion pairs and subsequent loss of the metal cation to the oxidant) is slow compared to the rate of the coupling reaction.

Tautomerism and Aromaticity in 1,2,3-Triazoles: The Case of Benzotriazole

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Abstract: This paper provides an explanation for the extraordinary difference in stability between 1,2,3-triazole and benzotriazole tautomers. In the gas phase, the 2*H* tautomer of 1,2,3-triazole represents more than 99.9% of the equilibrium mixture, whereas in benzotriazole the reverse is true (more than 99.99% of 1*H* tautomer at equilibrium). To understand the origin of this different behavior, an ab initio study at the 6-31G level was carried out on both tautomers of benzotriazole, on benzotriazolate anion, and on both tautomers of benzotriazolium cation (the 1,2- and the 1,3-*H*,*H*⁺ ions). Theoretical results (the proton affinity of 1*H*-benzotriazole is 10.2 kcal mol⁻¹ larger than that of 2*H*-benzotriazole) was checked against ICR measurements with excellent agreement (1-methylbenzotriazole is 10.4 kcal mol⁻¹ more basic than 2-methylbenzotriazole). Thermodynamic measurements (enthalpies of solution, vaporization, sublimation, and solvation) in three solvents (water, methanol, and dimethyl sulfoxide) confirm the predominance of the 1*H* tautomer in solution. Taking into account lone pair/lone pair repulsions and aromaticity, it is possible to explain the different behavior of 1,2,3-triazole and benzotriazole in the case of neutral molecules and their similarity in the case of protonated species.

In a preceding paper[1] the tautomerism of 1,2,3-triazole was approached both experimentally and theoretically. The main conclusions of that study were (i) theoretical calculations at the 6-31G level satisfactorily account for acid and basic properties of 1,2,3-triazole, (ii) in the gas phase, tautomer 2*H*-**2a** is more stable than tautomer 1*H*-**1a** by about 4.5 kcal mol⁻¹, (iii) in solution, tautomer **1a** becomes the most stable species because the large difference in dipole moments favors the more polar tautomer, **1a**, and (iv) triazolium ion **4a** is predicted to be more stable than **5a** by about 13.5 kcal mol⁻¹, which complicates the discussion of basicity data (**4a** cannot be obtained directly from **2a**).


1a   **2a**   **3a**   **4a**   **5a**
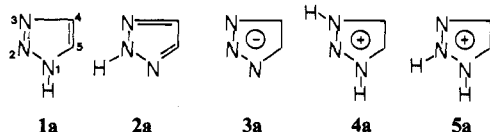
The origin of the lower stabilities of **1a** compared with **2a** and of **5a** compared with **4a** correspond to what we have termed "electrostatic proximity effects".[2] For neutral species, the effect corresponds to the lone pair/lone pair repulsion of adjacent

pyridine-like nitrogen atoms (N₂ and N₃ in **1a**) and for cations, to the repulsion between adjacent ⁺NH/⁺NH pairs (N₁H and N₂H in **5a**). We have estimated[2] both these effects to 6.5 kcal mol⁻¹.

Two very recent works confirm these findings. Begtrup et al.[3] studied the structure of 1,2,3-triazole by microwave spectroscopy, by gas-phase electron diffraction, and by ab initio calculations. Their experimental results (Table I) perfectly agree with our 6-31G*//6-31G calculations, and their ab initio calculations (basis set of double-ζ quality) give values close to those we obtained at the 6-31G//6-31G level. Anders et al.[4] found a difference in energy at the 6-31G*//6-31G* level that compares quite well with our 6-31G*//6-31G result (Table I).

In the present work, 6-31G//6-31G calculations on the corresponding benzotriazoles **1b–5b** will be reported together with experimental thermodynamic data involving these molecules, both in the gas phase and in aqueous solution.

1b   **2b**   **3b**

4b   **5b**
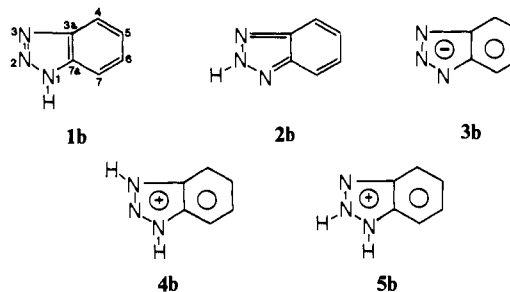
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