the electrophilic reagent RX to the reactive C center of an α-substituted (R′) oxime ether of this sort could yield predominantly one of the two possible products of opposite configuration at the α-carbon if the face selectivity were sufficiently large. Additional chelation by the donor atom in *E* results in tris-coordination of lithium; precoordination and syn entry of a reagent should not be impeded. The choice of the absolute configuration of the chiral auxiliary could then be used to predictively form CC bonds in a regio- and stereoselective fashion in the α-position of oxime ethers. If the entry of the electrophile occurs indeed in the suggested syn fashion, the approach of a prochiral reagent should be affected by the configuration of the chiral auxiliary, and stereoselective formation of two new asymmetric centers might be achieved.

Conclusions

Coordination isomerizations and racemizations of each of the syn- and the anti-configured ion pairs of acetaldoxime have been discussed in a systematic manner by examination of the number and the symmetries of the imaginary vibrational modes of the achiral (0,0) structures. Achiral structures that are minima would be intermediates for interconversion between any of the adjacent chiral minima. In the present case such achiral minima do not exist; the (0,0) structures are either transition-state structures or second-order saddle points. (0,0) structures with one imaginary frequency are transition-state structures for racemization, and the transition vector identifies the enantiomers that are interconverted. Two kinds of (0,0) second-order saddle points have been found. If none of the imaginary modes fulfills the in-plane displacement (IPD) condition, then the (0,0) structure is connected with two pairs of enantiomeric transition states for coordination isomerization. If one of the imaginary frequencies does fulfill the IPD condition, then there exists a pair of chiral transition states for one-step racemization. The racemization of **7b** provides an example of the latter case.

Ion pairing greatly facilitates rotations around the CC bond and the interconversion between geometrical isomers as compared to the free anions. All isomerizations of the ion pairs are found to have only small activation barriers. Thus, all of the isomeric ion pairs are readily available as building blocks for the thermodynamically most stable aggregates and as intermediates for reactions. Coordination isomerizations and racemizations involve either σ-type transition-state structures (1,4-(C,O)-σ- or 1,3-(N,C)-σ-bridged in the case of the syn- or the anti-configured ion pair, respectively) or transition-state structures in which the gegenion coordinates solely to the N_σ lone pair and the π-conjugation is maintained (π-type transition-state structures). The σ-type transition states involve rotation of the CH_2 group. The replacement of the HO group by an RO group is not expected to impede the rapid isomer interconversion seriously. The activation barrier for the one-step racemization of the NO-bond coordinated anti-configured ion pair would certainly be higher for metalated oxime ethers, but this racemization would still be possible via the pathway involving 2-fold coordination isomerization and racemization of the face-coordinated ion pair. However, alkoxy groups together with an alkyl substituent at the α-carbon should cause significant increases of the activation barriers for racemization. An α-substituent would probably increase the activation barrier for rotation around the CC bond substantially and such racemization pathways of the face-coordinated ion pairs may not be accessible. In these cases racemization via N-coordinated structures of the type **6d** may become important.

The long bond distances between the gegenion and the reactive carbon center and the facile interconversion between coordination isomers of the predominant syn-configured ion pair indicate that the entry of the electrophile from the metal-coordinated side should not be impeded. In contrast, such syn entry is likely to be favored over the anti entry as it allows prior coordination of the electrophile to the cation and ion-pair formation of the product. The chirality of the ion pairs could be exploited for regio- and stereoselective CC-bond formation at the α-carbon. Metalated oxime ethers with an enantiomerically pure chiral auxiliary in the alkoxy group could be used for this purpose if it were possible to design the alkoxy group in such a way as to assure face-coordination in the diastereoisomeric intermediate.

Finally, the solvation of the lithium has not been considered in the computations; however, the various stationary structures found can provide starting points for assessing qualitatively the effects of additional coordination to solvent in real examples in organic synthesis.

Acknowledgment. This research was supported in part by NIH Grant No. GM-30369. The calculations were carried out in part with computer time granted on the Cray II of the San Diego Supercomputer Center supported by NSF and on the VAX-8800 of the UC Berkeley Central Computer Facility. We are also indebted to Prof. S. Shatzmiller for important discussions.

Supplementary Material Available: *Z*-matrix forms, energies, and vibrational frequencies (and transition vectors) of the lithium ion pairs **6a–d** (syn), **7a–f** (anti), and **11** and of the sodium ion pairs **8a** and **8b** (syn) and **9a** and **9b** (anti) (13 pages). Ordering information is given on any current masthead page.

Theoretical Study of C_4O and C_6O

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Abstract: Ab initio calculations were performed which corroborate the interpretation of recent ESR data for C_4O and C_6O. Bond lengths, gross orbital spin populations, ${}^1\Sigma^+ - X{}^3\Sigma^-$ energy differences, stabilities, dipole moments, and vibrational frequencies were obtained from Hartree–Fock calculations. Electron correlation was included via second-, third-, and fourth-order many-body perturbation theory. Linear geometries were assumed in this study.

The C_4O and C_6O molecules have recently been observed by Van Zee, Smith, and Weltner (VSW) via electron spin resonance (ESR) in neon and argon matricies at 4 K.[1] VSW found these molecules to be triplet linear species with cumulene-like bonding, e.g. $:C{=}C{=}C{=}C{=}\ddot{O}:$. Also, the zero-field splitting parameter, $|D|$, was found to be larger for C_6O than for C_4O. This is similar to the increase in $|D|$ observed for the series C_4, C_6, and C_8 and was explained in the latter case by increasing spin–orbit contributions to $|D|$, by the first excited ${}^1\Sigma_g{}^+$ state, with increasing carbon chain length.[2]

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Table I. Structures of C_4O and C_6O (pm)[a]

C_6–C_5–C_4–C_3–C_2–C_1–O

	C_6C_5	C_5C_4	C_4C_3	C_3C_2	C_2C_1	CO
C_4O			130.9	127.7	128.5	114.5
C_6O	129.8	128.3	127.6	126.9	128.4	114.3

[a] HF/DZP; molecules assumed to be linear.

Table II. Electronic Configurations for the Ground States of C_nO Molecules

molecule	configuration	state
CO	$...4\sigma^2 1\pi^4 5\sigma^2$	$^1\Sigma^+$
C_2O[a]	$...6\sigma^2 1\pi^4 7\sigma^2 2\pi^2$	$^3\Sigma^-$
C_3O[b]	$...8\sigma^2 1\pi^4 9\sigma^2 2\pi^4$	$^1\Sigma^+$
C_4O[c]	$...10\sigma^2 1\pi^4 2\pi^4 11\sigma^2 3\pi^2$	$^3\Sigma^-$
C_5O[c]	$...12\sigma^2 1\pi^4 2\pi^4 13\sigma^2 3\pi^4$	$^1\Sigma^+$
C_6O[c]	$...14\sigma^2 1\pi^4 2\pi^4 3\pi^4 15\sigma^2 4\pi^2$	$^3\Sigma^-$

[a] Reference 8. [b] Reference 9. [c] Present work.

Ab initio molecular orbital calculations on C_4O and C_6O are reported here. The theoretical results corroborate the interpretation of the ESR data by VSW.

Methods

The present calculations were performed with the GAUSSIAN 86 system of programs.[3] Singlet states and states of higher multiplicity were investigated with the restricted (RHF) and unrestricted Hartree–Fock (UHF) methods, respectively. Electron correlation was included via many-body perturbation theory. Second- (MP2), third- (MP3), and fourth- (MP4) order many-body perturbation theory calculations were employed within the frozen-core approximation. The MP4 calculations included single, double, triple, and quadruple substitutions.

A double-ζ plus polarization (DZP) basis set was used for the calculations reported here. The basis set consists of Dunning's $(9,5)\rightarrow[4,2]$ double-ζ basis set,[4] augmented by six d orbitals on each atom. Each d orbital is a single-term Gaussian function with exponent equal to 0.75 for carbon and 0.85 for oxygen.

The notation advocated by Hehre et al. will be used here to indicate the theoretical model employed in a particular calculation.[5] For example, MP4/DZP//HF/DZP indicates that a MP4 calculation was done with the DZP basis set, at the geometry optimized with HF calculations which employed the same basis set. HF/DZP is taken to mean HF/DZP//HF/DZP.

Results and Discussion

The HF/DZP optimized bond lengths of C_4O and C_6O, assumed to be linear, are given in Table I. DZP basis sets are well-known to give bond lengths to within a few hundredths of an angstrom for most molecules. The nearly uniform carbon–carbon bond lengths indicate cumulene-like bonding, e.g. :C=C=C=C=Ö:. These bond lengths are quite similar to those of C_5O,[6] C_3O,[7] and C_2O.[8] Indeed, the carbon-carbon bond lengths of the C_nO series of molecules are very close to those of the C_n series.[10,11]

Various electronic configurations were tried at the HF/DZP level of theory in order to determine the ground states of C_4O and C_6O. These are given, and compared to the ground states of other C_nO molecules, in Table II. As in the C_n series,[12] a singlet/triplet alternation of ground spin states is observed for C_nO with odd/even numbers of carbon atoms. Furthermore, the ground-state electronic configurations of the C_nO molecules fit into a very regular pattern. Going from n to $n + 1$ adds four σ and two π electrons to the electronic structure. A previously half-filled π subshell becomes filled, giving a singlet. If species n is a singlet (all filled π subshells), species $n + 1$ adds a new, half-filled π subshell.

Table III. Gross Orbital Spin Populations (electrons) for C_4O and C_6O[a]

		p_π	p_σ	s	d
C_4O	C_4[b]	0.984	−0.027	0.052	0.016
	C_3	−0.004	−0.035	−0.015	0.017
	C_2	0.440	−0.013	0.054	0.004
	C_1	0.111	−0.021	−0.019	0.027
	O	0.411	0.000	0.020	−0.004
C_6O	C_6	0.901	−0.020	0.052	0.013
	C_5	−0.084	−0.032	−0.011	0.014
	C_4	0.314	0.004	0.029	−0.000
	C_3	−0.065	−0.023	−0.032	0.014
	C_2	0.410	−0.008	0.061	0.003
	C_1	0.094	−0.020	−0.018	0.024
	O	0.368	0.000	0.018	−0.004

[a] HF/DZP. [b] Numbering of carbon atoms is from the oxygen end of the molecules.

Table IV. Energy Difference (eV) between the Ground $^3\Sigma^-$ and Lowest $^1\Sigma^+$ States for C_4O and C_6O[a]

	HF/DZP	MP2/DZP// HF/DZP	MP3/DZP// HF/DZP
C_4O	1.412	0.381	0.469
C_6O	1.034	−0.104	0.110

[a] The $^1\Sigma^+$ state approximately calculated by the procedure of Magers et al., ref 16.

VSW concluded that the bonding in C_4O and C_6O is cumulene-like based on the small hyperfine splittings measured for these species. This would indicate that the unpaired spins are mainly p_π in character.[13] INDO calculations performed by VSW showed the spin density to indeed be mostly p_π. Table III gives ab initio gross orbital spin populations for C_4O and C_6O, calculated via a Mulliken population analysis.[14] The unpaired spins are seen to be mainly p_π in character, but unlike the INDO results the principal spin density lies on the terminal carbon atom. Both the ab initio and INDO calculations find oscillation of spin density along the chains. The many negative values reported in Table III arise from the fact that spin population is calculated as α (spin up) population minus β (spin down) population.

It is not evident from the spin populations given in Table III that the zero-field splitting for C_6O should be larger than that of C_4O. Perhaps the increase in $|D|$ with increasing carbon chain length can be explained by again considering the triplet, even n, C_n species.[2] There it was found that as carbon chain length increases, the difference in energy between the ground $^3\Sigma_g^-$ and lowest $^1\Sigma_g^+$ states decreases. The increase in $|D|$ was therefore attributed to increased spin–orbit contributions of the $^1\Sigma_g^+$ state, in analogy to the well-studied O_2 molecule.[15]

Table IV gives the energy difference between the ground $^3\Sigma^-$ and lowest $^1\Sigma^+$ states for C_4O and C_6O. At all levels of theory investigated the $^1\Sigma^+ - {}^3\Sigma^-$ energy gap for C_6O was found to be smaller than that of C_4O. The negative value in Table IV for C_6O at the MP2/DZP//HF/DZP level of theory indicates that the $^1\Sigma^+$ state lies lower than the $^3\Sigma^-$ state. This was also observed for C_6 and C_4.[2] It was pointed out there that MP2 calculations often overestimate singlet–triplet energy differences in favor of the singlet. At the MP3 level this overestimation is largely corrected.

The RHF singlet having the same configuration as a $^3\Sigma^-$ triplet is actually a mixture of the $^1\Sigma^+$ and $^1\Delta$ states. This was pointed

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Table V. Stabilities of C_nO Molecules (kcal/mol)

molecule	fragments	HF/DZP	MP4/DZP//HF/DZP
C_3O	C_2 + CO	129.7	79.3
C_4O	C_3 + CO	24.3	10.1
C_5O	C_2 + C_3O	168.1	121.5
C_6O	C_3 + C_3O	76.4	58.0
C_6O	C_5 + CO	32.3	891

Table VI. Dipole Moments (D) for C_nO Molecules[a]

molecule	HF/DZP	experiment
CO	−0.18	0.112[b]
C_2O	1.61	
C_3O	2.07	2.391[c]
C_4O	3.01	
C_5O	3.80	
C_6O	4.88	

[a] Negative sign indicates positive end of dipole is carbon end of molecule. [b] Reference 19. [c] Reference 20.

out by Magers et al. for linear C_4.[16] The method developed by Magers et al. for approximately removing the spin contamination from the $^1\Delta$ state, and then using this state to estimate the energy of the $^1\Sigma^+$ state, was used to calculate the $^1\Sigma^+ - {}^3\Sigma^-$ energy gaps given in Table IV. While Table IV clearly shows this energy gap to be smaller for C_6O than for C_4O, the numbers given are not quantitative. The wave functions are all single reference, and as discussed above, the different states were only sorted out approximately. Spin contamination of the triplets was not very large, being $\langle S^2 \rangle = 2.101$ for C_4O and 2.226 for C_6O (wave function corrected to first order).

VSW produced the C_nO molecules by photolysis in matricies containing C_n (from vaporization of graphite) and CO. The excitation wavelength used, 405 ± 20 nm, corresponds to the O–O band of the $^1\Pi_u \leftarrow X^1\Sigma_g^+$ system of C_3.[1] They concluded that C_4O is formed in the matrix via $C_3(^1\Pi_u) + CO(^1\Sigma^+) \rightarrow C_4O(^1\Pi) \rightsquigarrow C_4O(X^3\Sigma^-)$. They go on to speculate the C_6O is formed in a similar fashion from C_3 and C_3O, or perhaps from C_5 and CO.

Table V gives the stabilities of various C_nO molecules with respect to likely fragments (precursors) in their ground states. C_4O and C_6O are stable with respect to the precursors suggested by VSW. Zero-point energy corrections were not made, but these are expected to contribute only a few kilocalories per mole to the MP4 stabilites. The total MP4/DZP//HF/DZP energies for C_4O and C_6O are −226.821 128 and −302.760 923 au, respectively.

Table V also shows that C_3O and C_5O are more stable with respect to likely fragments than are C_4O and C_6O. Interstellar molecules containing linear carbon chains with odd numbers of carbon atoms are much more prevalent than those with even numbers of carbon atoms.[17] This suggests that species containing odd n linear C_n chains are more stable than those containing even n chains.

Pacchioni and Koutecky, using multireference CI calculations, find the $^1\Pi_u$ state of C_5 to lie 3.18 eV above the ground $^1\Sigma_g^+$ state.[18] This corresponds to the excitation wavelength used by VSW, so the formation of C_6O in the matrix from C_5 and CO may indeed be a possibility. This $^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition is predicted to be weak, however.[18]

The HF/DZP dipole moments for C_4O and C_6O are given in Table VI, where they are compared to other C_nO molecules and to available experimental values. HF/DZP dipole moments are seen to be too low by a few tenths of a debye. Dipole moment is seen to increase with increasing n for C_nO molecules. This is also the case for the HC_nN series.[21] Hence, as for long-chain HC_nN, the longer C_nO molecules may be observable in interstellar space even though their abundances are expected to be lower than shorter chain C_nO molecules. To date, C_3O is the only species of this series to have been observed.[22]

Table VII. HF/DZP Vibrational Frequencies (cm^{-1}) and Relative Intensities (in Parentheses) for C_4O

symmetry	unscaled	scaled[a]	experiment[b]
Π	134[c]	121	*d*
Π	419 (0.01)	377	*d*
Π	568 (0.02)	511	484.0 (0.06)
Σ	822[c]	740	774.8 (0.01)
Σ	1563[c]	1407	1431.5 (0.04)
Σ	2133 (0.16)	1920	1922.7 (0.65)
Σ	2443 (1.00)	2199	2221.7 (1.00)

[a] Scaling factor is 0.9. [b] Reference 23. [c] Relative intensity <0.01. [d] Not observed.

Table VIII. HF/DZP Vibrational Frequencies (cm^{-1}) and Relative Intensities (in Parentheses) for C_6O

symmetry	unscaled	scaled[a]
Π	82[b]	73
Π	201[b]	181
Π	401[b]	361
Π	528[b]	475
Π	583 (0.01)	525
Σ	601[b]	541
Σ	1173[b]	1056
Σ	1704 (0.03)	1533
Σ	2095 (0.03)	1885
Σ	2310 (0.08)	2079
Σ	2415 (1.00)	2174

[a] Scaling factor is 0.9. [b] Relative intensity <0.01.

Maier et al. have recently observed the IR spectrum of C_4O, which was produced when matrix-isolated C_5O_2 was irradiated with UV light at 230 nm.[23] HF/DZP vibrational frequencies, calculated with analytical second derivatives,[24] and relative intensities are given in Table VII, where they are compared to Maier's spectrum. The calculated frequencies are also shown in Table VII scaled by 0.9. HF/DZP stretching frequencies scaled by 0.9 have been shown for linear carbon molecules to be within 5% of experimental values, and typically lie below the experimental frequencies.[25] The error is generally greater for bending frequencies, since bending modes in these linear molecules are typically more anharmonic than are the stretching modes. HF/DZP intensities are only qualitative, being often more than 100% in error.[26] Table VII shows that Maier's assignment of this spectrum to C_4O is reasonable.

HF/DZP vibrational frequencies and relative intensities for C_6O are given in Table VIII, along with the HF/DZP scaled values. These should be helpful in assigning the vibrational spectrum of C_6O.

Acknowledgment. The author thanks Drs. B. E. Turner, R. J. Van Zee, and W. Weltner, Jr., for helpful discussions. The reviewers are thanked for their helpful comments. The Ohio Supercomputer Center is acknowledged for a grant of Cray time in support of this work.

Registry No. C_4O, 112022-61-4; C_6O, 112022-62-5.

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