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Structure and Energetics of Realistic Carbynes: (Carbohydroxy)carbyne (HOCOC:)

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Abstract: The carbyne HOC(=O)-C: has been examined theoretically as a model of the relative stable carbyne $\text{CH}_3\text{CH}_2\text{OCOC:}$: studied experimentally by Strausz, Skell, and co-workers. Ab initio electronic structure theory has been used to predict the geometrical structures and relative energies of three low-lying electronic states ($^2A'$, $^2A''$, and $^4A''$ in point group C_s). Both self-consistent-field and configuration interaction (up to 31 532 configurations treated variationally) methods were used in conjunction with double- ζ and double- ζ plus d basis sets. Of the three states, the $^2A''$ state is the ground state with the $^2A'$ state lying at 10 kcal and the $^4A''$ state at 17 kcal. Formally a single bond, the ground-state C—C: distance is predicted to be 1.503 Å, only slightly shorter than the standard value, 1.54 Å. The geometrical structures of the cis and trans conformers of each electronic state have been predicted, with the cis structures lying lower by 3–6 kcal in each case. An analogous theoretical analysis has been carried out for the isomer formoxycarbyne (HC(=O)O-C:), which is found to have rather different properties than (carbohydroxy)carbyne. For example, formoxycarbyne has a trans $^2A'$ ground state, with the $^2A''$ and $^4A''$ states lying at 12 and 70 kcal, respectively. Overall, formoxycarbyne is predicted to lie 25 kcal lower than (carbohydroxy)carbyne.

Monovalent carbon compounds, the carbynes R-C: , may logically be thought of as the most reactive of the four classes of compounds CR_4 , CR_3 , CR_2 , and CR , the latter having the highest degree of coordinative unsaturation. In fact, carbynes are so extremely reactive that it is often impossible to study the isolated molecules via spectroscopic techniques.¹ The only exceptions to this rule appear to be the simple diatomic carbynes^{2,3} CH , CF , CCl , CBr , and CI . Nevertheless, one may anticipate that with new technological advances, carbyne chemistry could develop in the last two decades of this century in much the same way as the study of carbenes⁴ has become an area of central importance to organic chemistry since 1950. Present interest in transition-metal carbynes⁵ [e.g., $(\text{CO})_4\text{ClCr}\equiv\text{CH}$] would appear to encourage such developments.

Although only the diatomic carbenes mentioned above have been characterized spectroscopically, it is possible to synthesize more complicated carbynes which have a considerably greater stability. The pioneering work in this area is represented by the 1974 paper of Strausz, Skell, and co-workers.⁶ They generated the relatively stable (carbethoxy)methyne (EtOCOC:) by the short wavelength photolysis of $(\text{N}_2\text{CCO}_2\text{Et})_2\text{Hg}$, bis(ethyl diazo-

acetato)mercury. Subsequent reactions with the olefins cyclohexene, *cis*-2-butene, and *trans*-2-butene were studied in detail. On the basis of observed stereospecificity of the cyclopropane-forming addition reactions, Strausz and Skell argued that the behavior of doublet ground-state carbynes parallels that of singlet carbenes. Further they postulated that excited quartet carbynes would react in a manner similar to triplet ground-state CH_2 , i.e., addition to olefins would be nonstereospecific and attack upon CH bonds would lead to abstraction rather than insertion. For the simplest carbyne reaction, namely, $\text{CH}(^2\Pi, ^4\Sigma^-) + \text{H}_2$, this simple picture has recently been verified in detail by theoretical methods.⁷

Although a good deal is known⁶ about the reaction of EtOCOC: , essentially nothing is known about the geometry, energetics, or electronic structure of this relatively stable of "realistic" carbynes. Such information would be particularly significant if it shed light on such issues as the doublet–quartet separation, whether the R-C: bond is a true single bond, and why this carbyne is significantly more stable than the prototype carbene CH . The present theoretical study aims to provide answers to these and other questions by using well-tested and reliable methods. The ethyl group in (carbethoxy)methyne is sufficiently distant from the carbyne C atom that a simplified model was adopted in which the C_2H_5 group is replaced by H. The actual system studied then is HOC(=O)-C: , which will be hereafter referred to as (carbohydroxy)carbyne. Since the analogous carbene HOC(=O)-CH has recently been studied⁸ by similar theoretical methods, a comparison between the two should also be of interest.

(1) See, for example, J. March, "Advanced Organic Chemistry", McGraw-Hill, New York, 1977, p 181.

(2) P. F. Zittel and W. C. Lineberger, *J. Chem. Phys.*, **65**, 1932 (1976).

(3) K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules", Van Nostrand Reinhold, New York, 1979.

(4) R. A. Moss and M. Jones, "Carbenes", Volume II, Wiley, New York, 1975.

(5) E. O. Fischer, *Adv. Organomet. Chem.*, **14**, 1 (1976).

(6) O. P. Strausz, G. J. A. Kennepohl, F. X. Garneau, T. DoMinh, B. Kim, S. Valenty, and P. S. Skell, *J. Am. Chem. Soc.*, **96**, 5723 (1974).

(7) B. R. Brooks and H. F. Schaefer, *J. Chem. Phys.*, **67**, 5146 (1977).

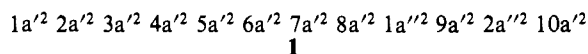
(8) K. S. Kim and H. F. Schaefer, *J. Am. Chem. Soc.*, **102**, 5389 (1980).

Table I. Technical Description of the Configuration Interaction (CI) Procedures Used in This Research

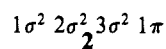
state	basis set	first CI procedure			second CI procedure		
		occupied orbitals frozen	virtual orbitals deleted	configurations	occupied orbitals frozen	virtual orbitals deleted	configurations
$^2A'$	DZ	6	6	10 360	4	4	19 107
	DZ + d	6	11	10 360	4	4	27 385
$^2A''$	DZ	6	6	9 950	4	4	18 231
	DZ + d	6	11	9 950	4	4	26 358
$^4A''$	DZ	6	6	12 134	4	4	21 989
	DZ + d	6	11	12 134	4	4	31 532

Electronic States of (Carbohydroxy)carbyne

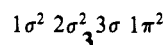
One of the simplest ways to think about the electronic structure of HOC(=O)C : is in terms of the two simpler molecules formic acid, HC(=O)O-H , and the prototype carbyne $\text{H-C}\cdot$. The merger of these two species may be thought in a sense to yield formoxycarbyne, an isomer of (carbohydroxy)carbyne. The ground-state electron configuration of formic acid is



and the lowest unoccupied molecular orbital (LUMO) is the $3a''$ or π^* orbital.⁹ For CH, the $^2\Pi$ ground state arises from

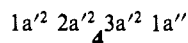


but the $^4\Sigma^-$ state, corresponding to electron configuration

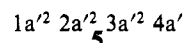


lies only 16.6 kcal higher.²

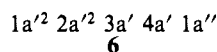
For a merger of the electronic structures of formic acid and CH, it is helpful to resolve¹⁰ the MO's of CH into the lower point group C_s . This yields for the $^2\Pi$ state



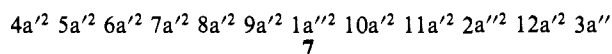
or



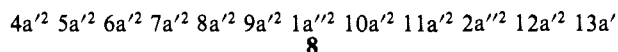
and for the $^4\Sigma^-$ state



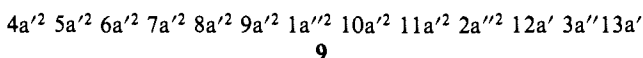
In forming $\text{HC(=O)O-C}\cdot$: from HC(=O)O-H and $\text{H-C}\cdot$, one O-H σ bond and one H-C : σ bond are replaced by a single O-C : σ bond. This argues for the removal of one of the occupied a' orbitals of the constituent parts. Thus combining **1** with **4** or **5** should yield two low-lying doublet states of formoxycarbyne [and (carbohydroxy)carbyne]



or



Similarly the lowest quartet state of formoxycarbyne should arise from the electron configuration



The above analysis suggests that the biggest difference between formoxycarbyne and the prototype CH is the existence of two

distinguishable doublet states ($^2A'$ and $^2A''$) for the former. Of course there are also two doublet states of CH (they might be labeled $^2\Pi_x$ and $^2\Pi_y$), but they are degenerate when the ordinary electrostatic Hamiltonian is adopted. In the case of formoxycarbyne and (carbohydroxy)carbyne, it should be interesting to see the structural differences between the $^2A'$ and $^2A''$ states.

Theoretical Details

The equilibrium geometrical structures for the $^2A'$, $^2A''$, and $^4A''$ states were determined at the self-consistent-field (SCF) level of theory by using a double- ζ basis set. The latter contracted Gaussian basis is of the standard Huzinaga-Dunning^{11,12} variety, labeled C,O(9s5p/4s2p), H(4s/2s), with the hydrogen s functions scaled by a factor of 1.2. Open-shell SCF gradient procedures¹³ proved extremely helpful in locating these three stationary points. In general, equilibrium geometries predicted by the DZ SCF method are reliable to a few hundredths of an angstrom (bond distances) and one or two degrees (angles), and the reader is referred to review articles^{14,15} for discussions on this point.

Given the DZ SCF equilibrium geometries, the effects of electron correlation were investigated by using the loop-driven graphical unitary group approach.^{16,17} The general procedure was to variationally incorporate all (Hartree-Fock interacting) configurations differing by one or two electrons from the $^2A'$, $^2A''$, and $^4A''$ reference configurations discussed in the previous sections. In practice, the size of the configuration interaction (CI) matrix may be significantly reduced by eliminating certain orbitals. Most obvious in this regard are the core of 1s-like basis functions, of which there are four occupied and four virtual for a DZ basis set. Even for a molecule as small as HOC(=O)C : however, there are 21 989 configurations for the $^4A''$ CI with four occupied and four virtual orbitals deleted. Therefore, in addition, calculations were carried out with six occupied and six virtual orbitals removed.

It is well-known¹⁸ that d functions on the carbon atom C in carbenes CR_2 are required to provide reliable predictions of the singlet-triplet energy separation. Analogous reasoning would suggest that doublet carbenes would be improperly treated relative to the comparable quartets without carbon d functions in the basis. Therefore, a second DZ + d basis was used with the understanding that d functions (Gaussian exponent 0.75) were added only to the carbene C atom. With this extension of the basis from 42 to 47 contracted Gaussian functions, of course, the size of the CI wave functions increases. The technical summary of the different types of correlated wave functions used here is given in Table I. The largest CI's, those for the $^4A''$ electronic states, involve 31 532

(11) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).

(12) T. H. Dunning, *J. Chem. Phys.*, **53**, 2821 (1970).

(13) J. D. Goddard, N. C. Handy, and H. F. Schaefer, *J. Chem. Phys.*, **71**, 1525 (1979).

(14) J. A. Pople, *Bull. Soc. Chim. Belg.*, **85**, 347 (1976).

(15) C. E. Dykstra and H. F. Schaefer, "The Chemistry of Ketenes, Allenes, and Related Compounds", S. Patai, Ed., Wiley-Interscience, Chichester, 1980, p 1.

(16) I. Shavitt, *Int. J. Quantum Chem. Symp.*, **11**, 131 (1977); **12**, 5 (1978).

(17) B. R. Brooks and H. F. Schaefer, *J. Chem. Phys.*, **70**, 5092 (1979); B. R. Brooks, W. D. Laidig, P. Saxe, N. C. Handy, and H. F. Schaefer, *Phys. Scr.*, **21**, 312 (1980).

(18) C. F. Bender, H. F. Schaefer, D. R. Franceschetti, and L. C. Allen, *J. Am. Chem. Soc.*, **94**, 6888 (1972).

(9) W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, 1973.

(10) G. Herzberg, "Electronic Structure of Polyatomic Molecules", Van Nostrand Reinhold, New York, 1966.

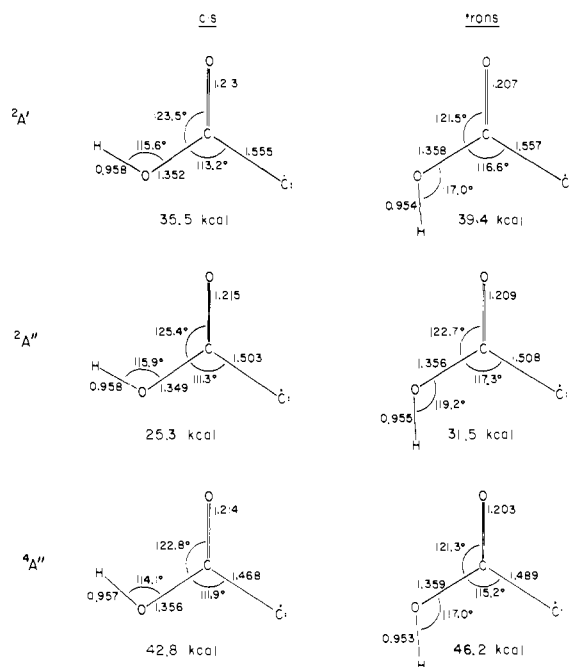
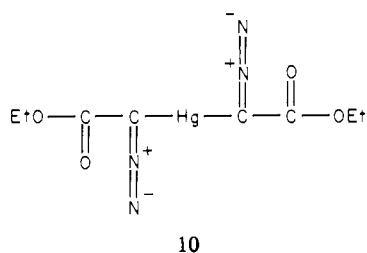


Figure 1. Predicted equilibrium geometries for the cis and trans isomers of (carbohydroxy)carbyne in their three lowest electronic states. All bond distances are in Å. Energies in kcal are relative to the trans ${}^2A'$ state of formoxycarbyne.

configurations. With the latest direct version of the loop-driven graphical unitary group approach, about 3 h is required for this task on the Harris 800 superminicomputer.

Equilibrium Geometries

The planar geometries determined for the ${}^2A'$, ${}^2A''$, and ${}^4A''$ states of $\text{HOC}(=\text{O})\dot{\text{C}}$: are seen in Figure 1. As we shall see, the ground state is the ${}^2A''$ state, which should therefore be considered first. As mentioned earlier, the critical issue is the degree to which the $\text{C}-\dot{\text{C}}$: bond is a true single bond. In this regard it is pertinent to note that a recent tabulation¹⁹ suggests that a "normal" $\text{C}-\text{C}$ single bond length is 1.54 Å. A specific comparison $\text{C}-\text{C}$ single bond distance related to HOCOC : is that recently determined²⁰ for bis(ethyl diazoacetato)mercury(II). The crystal



structure of Smith, Torres, and Strausz shows the $\text{C}-\text{C}$ single bond distances in **10** to be 1.45 ± 0.02 Å. This experimental result alerts us to the likelihood that the $\text{C}-\text{C}$ distance in our prototype carbyne may be considerably less than the standard 1.54-Å single bond value.

Figure 1 shows that all three electronic states have cis and trans minima on the potential surface. The cis and trans nomenclature here is based on the relationship between the H atom and the $\text{C}=\text{O}$ carbonyl bond. For the ${}^2A''$ ground state, the predicted $\text{C}-\text{C}$ bond distances are 1.503 (cis) and 1.508 Å (trans). Both distances are intermediate between the standard 1.54 Å $\text{C}-\text{C}$ single bond and the 1.45 ± 0.02 Å value observed²⁰ for **10**, bis(ethyl diazoacetato)mercury(II). Thus we view the $\text{C}-\text{C}$ bond in

(19) See S. H. Pine, J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry", McGraw-Hill, New York, 1980, p 86.

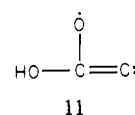
(20) R. A. Smith, M. Torres, and O. P. Strausz, *Can. J. Chem.*, **55**, 3527 (1977).

Table II. Relative Energies (kcal/mol) for (Carbohydroxy)carbyne,^a $\text{HOC}(=\text{O})\dot{\text{C}}$:

state	basis set	SCF	second CI procedure	
			variational	Davidson
cis ${}^2A'$	DZ	21.7	25.6	26.1
	DZ + d	30.4	34.7	[35.5]
trans ${}^2A'$	DZ	26.8	30.0	30.2
	DZ + d	35.5	39.0	[39.4]
cis ${}^2A''$	DZ	12.5	16.4	17.0
	DZ + d	19.9	24.5	[25.3]
trans ${}^2A''$	DZ	21.0	23.4	23.3
	DZ + d	28.5	31.4	[31.5]
cis ${}^4A''$	DZ	6.0	21.1	25.0
	DZ + d	19.0	38.1	[42.8]
trans ${}^4A''$	DZ	12.1	25.6	28.9
	DZ + d	25.2	42.4	[46.2]

^a For clarity, the most reliable level of theory is bracketed. Energies are given relative to the trans ${}^2A'$ ground state of formoxycarbyne, $\text{HC}(=\text{O})\dot{\text{C}}$:

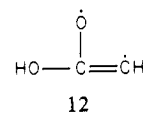
(carbohydroxy)carbyne as a "short single bond" rather than a "long double bond", as might be expected if a valence structure of the type



were significant.

The ${}^2A'$ state of $\text{HOC}(=\text{O})-\dot{\text{C}}$: the first excited electronic state, has a completely normal $\text{C}-\text{C}$ bond distance, 1.555 Å in the cis conformation, and 1.557 Å for the trans structure. However, the quartet carbyne shows considerable variation between the cis and trans structures. The cis $\text{C}-\text{C}$ distance of 1.468 Å is almost halfway from single to double CC bond, while the trans value is 0.021 Å longer and closer to that expected for a single $\text{C}-\text{C}$ bond. The only other point that must be made is that the HOC bond angles in Figure 1 are expected to be unrealistically large. This is commonly observed for ROR angles at the DZ SCF level of theory,²¹ and for H_2O the discrepancy²² between theory and experiment is 8.1°.

It is noteworthy that the $\text{C}-\dot{\text{C}}$: carbyne bond distances predicted here for all three electronic states are longer than the analogous $\text{C}-\text{C}$: carbene bond distance in (carbohydroxy)carbene,⁸ $\text{HOC}(=\text{O})\dot{\text{C}}\text{H}$. In the latter case the predicted ground-state triplet $\text{C}-\text{C}$: distance is 1.461 Å. This suggests that the carbene has somewhat more $\text{C}-\text{C}$ multiple bond character than the carbyne studied here. This fractional double bond character for the carbene could of course be accounted for by a contribution from the valence structure



Finally, it should be mentioned that the $\text{C}-\text{C}$: distance in singlet (carbohydroxy)carbene is 1.470 Å or only slightly longer than the triplet distance discussed above.

Energetics

The relative energies of the different conformers and electronic states of $\text{HOC}(=\text{O})\dot{\text{C}}$: are given in Table II. At the SCF level of theory the cis ${}^4A''$ quartet state is predicted to lie lowest. However, configuration interaction (CI) with either the DZ or

(21) J. E. Boggs and F. R. Cordell, "Accurate *Ab Initio* Gradient Calculation of the Structures and Conformations of Some Boric and Fluoroboric Acids. Basis Set Effects on Angles Around Oxygen", to be published.

(22) T. H. Dunning, R. M. Pitzer, and S. Aung, *J. Chem. Phys.*, **57**, 5044 (1972).

Table III. Relative Energies, Predicted at Various Levels of Theory, for Formoxycarbyne,^a HC(=O)OĈ:

	state	basis set	SCF	first CI procedure		second CI procedure	
				variational	Davidson	variational	Davidson
cis	² A'	DZ	-0.5	0.1	0.3	0.3	0.5
		DZ + d	0.8	1.0	1.1	1.7	[1.8]
trans	² A'	DZ	0.0	0.0	0.0	0.0	0.0
		DZ + d	0.0	0.0	0.0	0.0	[0.0]
cis	² A''	DZ	7.5	9.0	9.1	9.2	9.4
		DZ + d	10.1	10.9	10.9	12.1	[12.3]
trans	² A''	DZ	(15.1) ^b				
cis	⁴ A''	DZ	36.7	51.8	55.3	50.8	54.5
		DZ + d	44.0	59.3	62.7	64.7	[69.6]
trans	⁴ A''	DZ	41.8	56.5	59.8	55.2	58.7
		DZ + d	48.5	63.2	66.4	68.3	[73.0]

^a All energies are in kcal/mol. For clarity, the most reliable level of theory is bracketed. ^b Not a minimum on the potential-energy hypersurface.

DZ + d basis predicts the cis conformer of the ²A'' state to lie lowest. The nonvariational Davidson correction²³ for quadruple excitation correlation effects reinforces this view. The final theoretical prediction is for a ground ²A'' state, with the ²A' state lying 10.1 kcal higher and the ⁴A'' state 17.4 kcal above the ground state. The importance of correlation effects is seen from the fact that the DZ + d SCF ²A''-⁴A'' separation is -0.9 kcal, while the DZ + d correlated prediction is +17.4 kcal. Similarly d functions lower the ²A'' state relative to ⁴A'' by 5.6 kcal at the SCF level and 9.4 kcal with the Davidson corrected CI. In this respect the doublet carbyne-singlet carbene analogy is a very good one.¹⁸

Figure 1 and Table II show the cis conformation to be energetically favored for each of the three carbyne electronic states. The cis-trans energy differences are predicted to be 6.1 kcal (²A''), 3.9 kcal (²A'), and 3.4 kcal (⁴A''), all reasonable values for rotation about a C-O single bond. For example, the barrier for rotation about the OH bond in the related acetic acid molecule (HOC(=O)CH₃) is ~8 kcal.²³ For the analogous carbene, (carbohydroxy)carbene, the barrier to rotation about OH is quite similar, 7.7 kcal.⁸ Finally, Figure 1 shows that in each case the C-O bond distance increases (by 0.007, 0.006, and 0.003 Å) in going from the cis to the energetically less favorable trans form.

Formoxycarbyne: A Closely Related Isomer

As noted in the section "Electronic States of (Carbohydroxy)carbyne", the molecules HOC(=O)Ĉ: [(carbohydroxy)carbyne] and HC(=O)OĈ: (formoxycarbyne) are closely related isomers. Therefore a completely analogous theoretical study of formic carbyne was undertaken, with the results summarized in Figure 2 and Table III. These results are especially interesting in that they are very different from the analogous predictions for (carbohydroxy)carbyne.

It should be noted first that the two lowest electronic states of formoxycarbyne both lie energetically below the ground state of (carbohydroxy)carbyne. Specifically, the ground ²A'' state of HC(=O)OĈ: lies 25.3 kcal below the ground ²A' state of HOC(=O)Ĉ:. Moreover, the energetic ordering of the ²A' and ²A'' states is reversed between the two carbyne isomers. Furthermore, the favoring of the cis conformers of HOC(=O)Ĉ: is reversed for HC(=O)OĈ:, with the trans ²A' form being the lowest energetically. Finally, the doublet-quartet separation in formoxycarbyne (73.0 kcal) is much greater than that in (carbohydroxy)carbyne (17.4 kcal). One is forced to the inescapable conclusion that the HC(=O)O— and HOC(=O)— ligands have very different electronic properties.

Perhaps the simplest explanation of the difference in doublet-quartet energy separation between HOC(=O)Ĉ: and HC(=O)OĈ: substitutes formyl carbyne (HC(=O)Ĉ:) for the former and hydroxycarbyne (HO—Ĉ:) for the latter. The replacement of HOC(=O)— with HC(=O)— and of HC(=O)O— with HO— would appear to be correct in a simple picture. Reference to Hoffmann's classic work on carbenes²⁴ and to more detailed

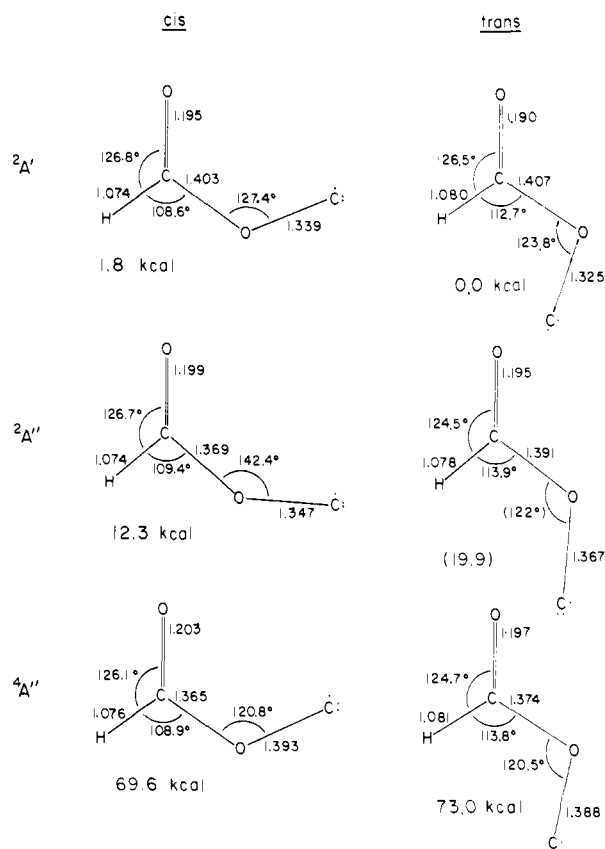


Figure 2. Predicted equilibrium geometries for the cis and trans isomers of formoxycarbyne, with bond distances in Å. Note that the trans ²A'' state is not a true minimum on the C₂O₂H potential-energy hypersurface. The COC angle has been constrained as 122° and the energy minimized with respect to the other geometrical parameters.

theoretical studies^{25,26} then shows that the hydroxy ligand stabilizes singlet (vs. triplet) carbenes while the formyl ligand has a relatively neutral effect on singlet-triplet separations. Intuitively speaking, the HO ligand is a σ acceptor and π donor. As noted by Baird and Taylor,²⁶ singlet stabilization energies in HĈX are in general agreement with the magnitude of the interaction between the p_x lone pair on X and the empty p_x orbital on Ĉ. For the formyl substituent, normally thought to be electron withdrawing, the π donor- π acceptor situation is much more ambiguous, and a clear prediction is not always possible.²⁷

(24) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Am. Chem. Soc.*, **90**, 1485 (1968); R. Gleiter and R. Hoffmann, *ibid.* **90**, 5457 (1968).

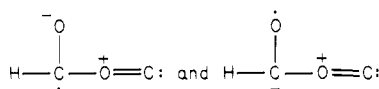
(25) R. R. Lucchese and H. F. Schaefer, *J. Am. Chem. Soc.*, **99**, 13 (1977); **100**, 298 (1978).

(26) N. C. Baird and K. F. Taylor, *J. Am. Chem. Soc.*, **100**, 1333 (1978).

(27) M. N. Paddon-Row, C. Santiago, and K. N. Houk, *J. Am. Chem. Soc.*, **102**, 6561 (1980).

(23) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *Aust. J. Chem.*, **25**, 1601 (1972).

Formoxycarbyne is a genuine carbyne in the sense that the carbyne carbon appears to be splendidly monovalent. The O–C: distance for the trans $^2A'$ structure is 1.325 Å, quite close to that in formic acid¹⁰ HC(=O)—OH (namely 1.343 Å) but shorter than the standard C–O single bond distance¹⁹ in methanol, 1.43 Å. Thus there is some support for contributions from valence structures of the form



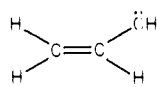
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The O–C: distances in the higher lying $^2A''$ and $^4A''$ state are somewhat longer, confirming the diminishing double-bond character.

Finally, it should be mentioned that the trans $^2A''$ structure of formoxycarbyne is not a relative minimum on the potential-energy hypersurface. The geometry illustrated in Figure 2 was obtained by constraining the COC angle to be 122°, approximately the average between the $^2A'$ and $^4A''$ equilibrium values. If this COC angle is unconstrained, it is observed to monotonically increase to linearity (180°) and then continues to the cis equilibrium value. At the DZ SCF level of theory, Table II shows that the constrained trans structure lies 7.6 kcal above the cis equilibrium.

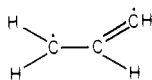
Bond-Shifted Isomers

It should be pointed out here that for some analogous unsaturated carbenes, there exists the possibility of what might be called bond-shifted isomers. For example, for vinylmethylene,²⁸ the expected equilibrium structure is



14

while second isomer with the same atomic connectedness would be



15

Similar problems have been discussed for cyanomethylene²⁹ and the vinyloxy radical³⁰ and in a more general context by Davidson.³¹

(28) J. H. Davis, W. A. Goddard, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 2427 (1977).

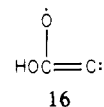
(29) J. F. Harrison, A. Dendramis, and G. E. Leroi, *J. Am. Chem. Soc.*, **100**, 4352 (1978); M. E. Zandler, J. D. Goddard, and H. F. Schaefer, *ibid.*, **101**, 1072 (1979).

(30) M. Dupuis, J. J. Wendeloski, and W. A. Lester, *J. Chem. Phys.*, in press.

(31) E. R. Davidson, "Singlet-Triplet Energy Separation in Carbenes and Related Molecules", to be published.

In several cases it was concluded that low levels of theory can be quite misleading with respect to the ultimate prediction of the energy difference between such bond-shifted isomers.

Although these considerations do not apply to formoxycarbyne, they do suggest the existence of a bond-shifted isomer of (carbohydroxy)carbyne, namely,



16

However, at the DZ restricted SCF level of theory, structure **16** is apparently not a distinct minimum on the $^2A''$ C₂O₂H potential-energy hypersurface. The word apparently is used here because it is very difficult to rule out the existence of a minimum of type **16** separated by a barrier of perhaps 0.1 kcal from the lower energy carbyne. In addition we must be careful not to preclude the possibility that structure **16** might become a minimum at some higher level of theory.

Concluding Remarks

The (carbohydroxy)carbyne molecule (HOC(=O) \dot{C} :) studied here theoretically is expected to bear a close resemblance to the experimentally characterized (carbohydroxy)carbyne EtOC(=O) \dot{C} : molecule of Strausz and Skell.⁶ Since the quartet carbyne is predicted to lie ~17 kcal above the lowest doublet electronic state and is expected to be significantly less reactive than the doublet, the nonobservance of the former is not surprising. The predicted doublet-quartet separation for (carbohydroxy)carbene is very similar to the experimental value 16.6 kcal of Zittel and Lineberger for the parent CH. This and an independent comparison⁸ between HOC(=O)— $\dot{\text{C}}\text{H}$ and CH₂ suggest that the HOC(=O)—ligand (carbohydroxy) has relatively little effect on intersystem energy differences when replacing a H atom. If anything, the carbohydroxy ligand would appear to lower a singlet carbene (doublet carbyne) by 1 or 2 kcal relative to the analogous triplet (quartet) state.

In essentially every respect, the Strausz-Skell analogy between doublet carbynes and singlet carbenes is confirmed here. A particularly challenging experimental task would be the preparation and mechanistic study of a carbyne having a quartet ground state, since most carbynes will undoubtedly be doublet ground states. The Li– $\dot{\text{C}}$: molecule would probably be a quartet,³² certainly to the degree that it has Li⁺C⁻ character (atomic C⁻ has a ^4S ground state). Hopefully some other quartet carbyne, more suitable for kinetic studies, can be prepared in the laboratory.

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Registry No. (Carbohydroxy)carbyne, 69098-12-0; formoxycarbyne, 80532-49-6.

(32) P. E. Cade and W. H. Huo, *At. Data Nucl. Data Tables*, **15**, 1 (1975).