of the σ bond are given in Figure 3a (these orbitals have an overlap of 0.79, typical of a σ bond). As the bond is dissociated, the left orbital becomes Ni 4s while the right orbital becomes $\sigma(CH_2)$. At R_e the hybridization of these orbitals is Ni $4s^1 4p^{0.034} 3d^{0.25}$ and C $2s^1 2p^{1.52} 3d^{0.014}$, respectively. The orbitals of the π bond are shown in Figure 3b (they have an overlap of 0.25). Here the hybridizations are Ni $3d^1 4p^{0.0002}$ and C $2p^1 3d^{0.0005}$, respectively. The self-consistent Ni dσ and dπ^+ orbitals are shown in Figure 3cd; they interact only weakly with the CH_2 group. The dδ^+ and dδ^- orbitals are quite atomic-like and are not shown. THE CH bond pairs (only one is shown) are quite similar to the CH bond pairs of CH_2 (the carbon hybridization is $2s^1 2p^{1.88} 3d^{0.0069}$).

The total charge transfer from Ni to CH_2 is 0.56 electrons for $^1A_1$ (dπ^-) and 0.51 electrons for $^3A_2$ (dδ^+)(both based on Mulliken populations).

Because of the small overlap of the two orbitals in the π bond, HF calculations do extremely badly for the $^1A_1$ (dπ^-) state. Consequently HF leads to a $^3A_2$ (dδ^+) ground state and puts the correct ground state, $^1A_1$, 3.8 eV higher. Clearly, HF is not adequate for studying transition metal-carbene systems.

In summary we find that Ni=CH_2 and Ni—CH_3 lead to bond energies of 65 and 60 kcal, bond lengths of 1.78 and 1.87 Å, and NiCH bond angles of 123.5° and 109.4°, respectively. In both cases the bonding is basically that of an Ni 4s orbital and a carbon lobe orbital with only a small contribution due to π bonding in $NiCH_2$. Although the numbers are consistent with general ideas about metal-carbon bonds, there is little information with which to compare experimentally.[15]

References and Notes

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Localized Molecular Orbitals for Cumulenes. Three-Center Bonds, Fractional Bonds, and Bending Force Constants

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Abstract: PRDDO wave functions were localized using the criterion of Boys for C_nO_2 (n = 1, 3, 5, 7), C_n (n = 3, 5, 7), H_2C_nO (n = 1, 2, 4, 6), and $H_2C_nH_2$ (n = 2, 3, 5, 7). Ab initio wave functions were localized using the criterion of Edmiston and Ruedenberg for C_3 and ketene. The two localization criteria produced nearly identical results for C_3, but different results for ketene, the principal difference being the representation of the CO linkage. Three-center CCC bonds rather than cumulated double bonds are found in C_nO_2 and C_n molecules. Cumulated double bonds were found in H_2C_nO and the $H_2C_nH_2$ molecules. In C_nO_2, H_2C_nO, and C_n ($n > 3$) fractional bonds to carbon (inherently delocalized LMO's) are found. The localized molecular orbitals (LMO's) fall into simple patterns, most easily understood if the σ and π orbitals are localized separately. Both CCC bending and CH_2 out-of-plane bending are discussed and interpreted in the context of localized orbitals. Bond indices, valencies, and atomic charges are also reported. Soft bending potentials are associated with three-center CCC bonds and with significant negative atomic charges. High bending force constants are associated with fractionally bonded carbons and positive atomic charges.

The structure of carbon suboxide, an oxycumulene, has been a subject of both experimental and theoretical interest for over 40 years. Both linear and bent structures have been proposed.[1-7] The anharmonic nature of the CCC bending potential is now accepted as the correct explanation for the anomalies in the spectra of carbon suboxide.[2,3,7-11] A double-minimum potential favoring a CCC angle of ca. 160° and having a barrier to the linear configuration less than the lowest vibrational energy level is indicated by recent work.[2,3] Both semiempirical[12-14] and ab initio[4-7,15-19] treatments of carbon suboxide have appeared. The slight hump in the potential for the linear configuration is elusive and appears to require the use of d orbitals or the basis sets used by Christoffersen et al.[6] based on floating spherical Gaussian orbitals to be detected. Calculations using a large, polarized basis set have produced an anharmonic bending potential with a single minimum, the linear form.[7] Christoffersen's molecular fragments method yielded a bending potential with minima for a CCC angle of 125° and CCO angles of 176° in a zigzag conformation. This method appears to exaggerate the size of the barrier to linearization.[6]

The C_3 molecule has been the subject of experimental and theoretical interest for over 30 years.[20-27] Experimental results indicate a low bending frequency, $\nu_2 = 64\ \mathrm{cm}^{-1}$.[27b] Although C_3 appears to be linear, a slight potential maximum for the linear configuration is not yet ruled out by experiment if the barrier is less than the lowest vibrational energy level.[24,27b] Calculations using a 4s2p1d basis set have produced a bent structure with a bond angle of 125°.[24] Calculations using a 4s3p1d basis set have produced a distinctly anharmonic potential with a single minimum. This latter calculation was in better overall agreement with experimental results.[24] Thus the CCC bending potential in C_3, like that in carbon suboxide, is quite anharmonic and requires large, flexible basis sets to be accurately described. Electron correlation for the C_3 molecule at least does not appear to affect critically the bending potential.[24]

For both C_3O_2 and C_3, the traditional representations of electronic structure (or the most important valence bond structure) have cumulated double bonds.[28] For both molecules, however, considerable resonance is indicated.[1,13] To date no localized molecular orbital structures have been published for either molecule. Localization of molecular orbitals transforms the delocalized canonical molecular orbitals (CMO's) of MO theory into the localized bond pairs, lone pairs, and inner shells of the Lewis theory and of chemical intuition.[29-33] However, localized molecular orbital (LMO) structures do not always coincide with simple Lewis structures, especially when several resonance structures are important,[34-36] as in the case at hand.

Recently the LMO structure of CO_2, the simplest oxycumulene, was reported.[35] The extension of this work to other cumulenes was undertaken to explore the nature of localized (or delocalized) bonding in C_3O_2 and to compare the LMO's for a series of related cumulenes. The molecules chosen for study were C_nO_2 (n = 1, 3, 5, 7), C_n (n = 3, 5, 7), H_2C_nO (n = 1, 2, 4, 6), and H_4C_n (n = 2, 3, 5, 7). Molecular orbitals were also localized for CO and H_2C_2 for purposes of comparison, as these molecules have CO and CC triple bonds. The even members of the C_nO_2 series are expected to be unstable as singlets, though C_2O_2 has been shown to be stable with respect to dissociation as a triplet.[37] The even members of the C_n series have open shells for $n > 2$.[21-22]

Methods

The wave functions used in this study, with three exceptions, were obtained using the PRDDO method.[38] This procedure is an approximate, nonempirical SCF method using a minimum basis set of Slater-type orbitals. PRDDO results have been shown to be of nearly ab initio quality for minimum basis set calculations. The efficiency of the method is such that a large number of related molecules can be studied at the same level of approximation without prohibitive expense.[38c] In three instances, the C_3 molecule, ketene, and a bent configuration of carbon dioxide, an ab initio minimum basis set wave function[39] was obtained in addition to the PRDDO wave function. Pople's standard molecular exponents[40] were used throughout this study.

Localizations were performed using the criterion of Boys[41] (maximum separation of orbital centroids), and for the ab initio wave functions, the criterion of Edmiston and Ruedenberg[42] (maximum self-repulsion energy). Localizations were carried out both with and without the constraint of σ-π separation. We term the former a σ-π localization, and the latter a complete localization.

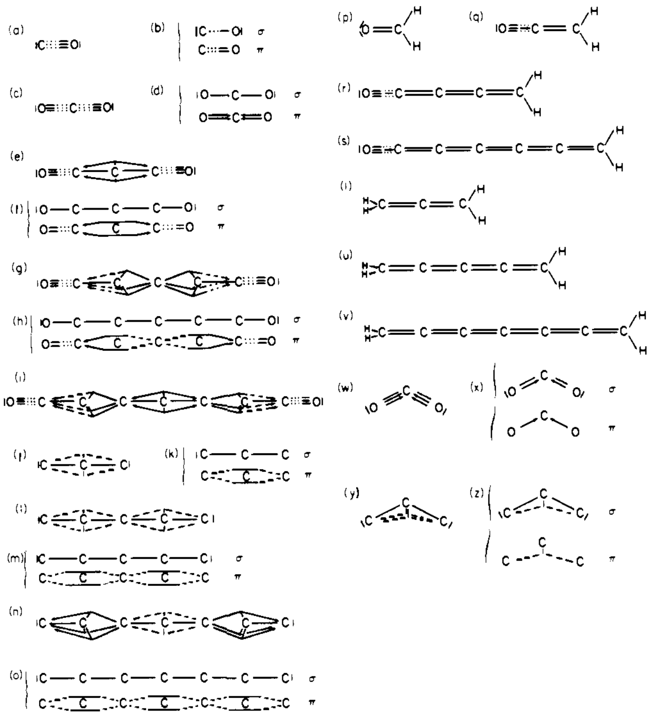


Figure 1. Boys localizations using the notation in Table II: parts a, c, e, g, i, j, l, n, p–v, w, and y, complete localizations; parts b, d, f, h, k, m, o, x, and z, σ-π localizations; parts w–z, bent geometries. See Tables I and II.

Valencies and bond indices were calculated by the method of Armstrong, Perkins, and Stewart.[43] They define the valency V_a of atom a as the sum of the indices of bonding, B_{ab}, between atom a and all other atoms, b, i.e.,

$$V_a = \sum_{a \neq b} B_{ab} = \sum_{a \neq b} \sum_{i_a} \sum_{j_b} (P_{i_a j_b})^2$$

where B_{ab} is obtained from the squares of the elements of the density matrix p over orthogonalized atomic orbitals. The sums extend over all orthogonalized AO's i on center a, and j on center b. Mulliken atomic charges[44] were also calculated.

Experimental bond lengths were used for CO,[45] H_2CO,[46] CO_2,[47] C_3,[48] H_2C_2,[49] C_3O_2,[2] H_2C_2O,[50] H_4C_2,[51] and H_4C_3.[52] Bond lengths for the higher homologues were taken from the lower members of the series. For CCC and OCC bending, individual bond angles were varied with the rest of the molecular geometry remaining fixed with linear angles. For C_3O_2[7,15] and C_3[24] large basis set studies have shown that the bond distances are relatively insensitive to CCC bending. For out-of-plane bending, HCH angles were optimized using a quadratic prediction of the minimum for each out-of-plane angle with bond distances and the remaining bond angles remaining fixed.

Results

The results of the localizations for the linear molecular configurations are shown in Table I and in Figure 1 using the line notation summarized in Table II. Localizations for C_3 and CO_2 with central angles of 125° are also shown in Table I and Figure 1, as is a localization of ketene with an out-of-plane angle of 55°. The numbering of the atoms is indicated in Figure 2.

Except as required by symmetry, no multiple maxima were found on the localization surfaces. A limited second-derivative test[33b] was performed to analyze the curvature of the LMO hypersurface. This test allowed us to verify that the structures reported were indeed maxima on the localization surfaces. However, the Boys localization surfaces are flat (i.e., the localizations are indeterminate) in regard to the rotation of any

Table I. Localized Molecular Orbitals[a]

		Atom			Populations			% s character			% delocal-ization[b]
Localization	Orbital	A	B	C	A	B	C	A	B	C	
CO σ-π	Lone pair	O(1)			2.05			72			12
		C(1)			2.01			76			11
	σ bond	O(1)	C(1)		1.31	0.69		33	31		0
	π bond	O(1)	C(1)		1.44	0.56		0	0		0
CO complete	Lone pair	O(1)			2.00			64			16
		C(1)			2.00			75			14
	τ bond	O(1)	C(1)		1.41	0.59		15	11		0
CO_2 σ-π	Lone pair	O(1)			2.05			81			17
	σ bond	O(1)	C(1)		1.07	0.93		23	57		3
	π bond	O(1)	C(1)		1.54	0.44		0	0		12
CO_2 complete	Lone pair	O(1)			1.98			74			23
	τ bond	O(1)	C(1)		1.41	0.58		10	23		10
C_3O_2 σ-π	Lone pair	O(1)			2.05			79			16
	σ bond	O(1)	C(1)		1.15	0.85		26	52		3
		C(1)	C(2)		1.13	0.87		58	53		6
	π bond	O(1)	C(1)		1.47	0.52		0	0		9
		C(1)	C(2)	C(3)	0.32	1.26	0.32	0	0	0	20
C_3O_2 complete	Lone pair	O(1)			1.99			72			21
	τ bond	O(1)	C(1)		1.38	0.61		11	18		8
		C(1)	C(2)		1.08	0.89		55	44		10
		C(1)	C(2)	C(3)	0.34	1.25	0.34	4	4	4	19
C_5O_2 σ-π	Lone pair	O(1)			2.05			79			16
	σ bond	O(1)	C(1)		1.16	0.85		26	52		3
		C(1)	C(2)		1.14	0.87		58	51		5
		C(2)	C(3)		0.95	1.06		55	53		5
	π bond	O(1)	C(1)		1.45	0.54		0	0		9
		C(1)	C(2)	C(3)	0.30	1.20	0.41	0	0	0	19
C_5O_2 complete	Lone pair	O(1)			1.99			72			20
	τ bond	O(1)	C(1)		1.37	0.62		11	18		7
		C(1)	C(2)		1.13	0.86		56	41		9
		C(1)	C(2)	C(3)	0.20	1.12	0.62	0	14	27	16
C_7O_2 complete	Lone pair	O(1)			1.99			72			20
	τ bond	O(1)	C(1)		1.36	0.63		11	18		7
		C(1)	C(2)		1.13	0.86		56	41		9
		C(3)	C(4)		1.01	0.96		50	44		10
		C(1)	C(2)	C(3)	0.19	1.11	0.64	0	14	27	16
		C(3)	C(4)	C(5)	0.39	1.14	0.39	4	5	4	19
C_3 σ-π	Lone pair	C(1)			2.02			71			10
	σ bond	C(1)	C(2)		0.96	1.05		30	54		4
	π bond	C(1)	C(2)	C(3)	0.42	1.17	0.42	0	0	0	0
C_3 ER σ-π	Lone pair	C(1)			2.03			74			12
	σ bond	C(1)	C(2)		0.96	1.04		30	51		3
	π bond	C(1)	C(2)	C(3)	0.42	1.16	0.42	0	0	0	0
C_3 complete	Lone pair	C(1)			2.02			71			10
	τ bond	C(1)	C(2)		0.90	1.06		30	41		10
		C(1)	C(2)	C(3)	0.42	1.16	0.42	3	8	3	0
C_3 ER complete	Lone pair	C(1)			2.03			73			12
	τ bond	C(1)	C(2)		0.91	1.05		29	39		10
		C(1)	C(2)	C(3)	0.43	1.15	0.43	3	7	3	0
C_5 σ-π	Lone pair	C(1)			2.02			73			11
	σ bond	C(1)	C(2)		0.94	1.07		29	58		5
		C(2)	C(3)		0.93	1.08		49	52		5
	π bond	C(1)	C(2)	C(3)	0.42	1.15	0.40	0	0	0	12
C_5 complete	Lone pair	C(1)			2.02			72			11
	τ bond	C(1)	C(2)		0.92	1.06		29	48		9
		C(2)	C(3)		0.98	0.93	[c]	30	46		15
		C(1)	C(2)	C(3)	0.38	1.13	0.46	1	7	11	11
C_7 σ-π	Lone pair	C(1)			2.02			73			11
	σ bond	C(1)	C(2)		0.94	1.07		29	58		5
		C(2)	C(3)		0.94	1.07		49	53		5
		C(3)	C(4)		1.06	0.95		51	52		5
	π bond	C(1)	C(2)	C(3)	0.41	1.14	0.41	0	0	0	12
		C(3)	C(4)	C(5)	0.39	1.13	0.39	0	0	0	18
C_7 complete	Lone pair	C(1)			2.02			73			11
	τ bond	C(1)	C(2)		0.93	1.06		29	48		9
		C(3)	C(4)		1.01	0.96		48	43		10
		C(1)	C(2)	C(3)	0.28	1.07	0.62	0	14	28	10
		C(3)	C(4)	C(5)	0.40	1.12	0.40	4	6	4	18
OCH_2 complete	Lone pair	O(1)			1.98			42			12
	τ bond	O(1)	C(1)		1.13	0.88		12	18		3
	Single bond	C(1)	H(1)		1.06	0.96		39			12
OC_2H_2 σ-π	Lone pair	O(1)			2.02			74			18
	τ bond	O(1)	C(1)		1.22	0.78		17	23		4
	σ bond	C(1)	C(2)		1.19	0.82		58	30		9

Table I (*Continued*)

Localization	Orbital	Atom			Populations			% s character			% delocalization[b]
		A	B	C	A	B	C	A	B	C	
	Single bond	C(2)	H(1)		1.07	0.93		40			9
	π bond	O(1)	C(1)		1.72	0.25		0	0		11
		C(1)	C(2)		0.72	1.26		0	0		14
OC_2H_2 ER $\sigma-\pi$	Lone pair	O(1)			1.99			71			21
	τ bond	O(1)	C(1)		1.24	0.76		21	18		4
	σ bond	C(1)	C(2)		1.22	0.80		59	30		9
	Single bond	C(1)	H(1)		1.07	0.93		40			9
	π bond	O(1)	C(1)		1.72	0.22		0	0		15
		C(1)	C(2)		0.74	1.26		0	0		10
OC_2H_2 complete	Lone pair	O(1)			1.98			69			20
	τ bond	O(1)	C(1)		1.24	0.75		12	20		5
		O(1)	C(1)		1.72	0.26		15	4		10
		C(1)	C(2)		0.96	1.04		34	10		11
	Single bond	C(2)	H(1)		1.07	0.93		38			10
OC_2H_2 ER complete	Lone pair	O(1)			1.89	[d]		45			18
	τ bond	C(1)	C(2)		1.00	1.02		35	10		7
		O(1)	C(1)		1.21	0.79		10	20		4
	Single bond	C(2)	H(1)		1.07	0.93		38			10
OC_4H_2 complete	Lone pair	O(1)			1.99			71			20
	τ bond	O(1)	C(1)		1.27	0.72		12	20		6
		O(1)	C(1)		1.61	0.37		11	12		10
		C(1)	C(2)		0.88	1.05	[e]	33	16		14
		C(2)	C(3)		1.03	0.91	[f]	23	26		12
		C(3)	C(4)		1.00	1.00		28	14		8
	Single bond	C(4)	H(1)		1.07	0.93		37			9
OC_6H_2 complete	Lone pair	O(1)			1.99			71			20
	τ bond	O(1)	C(1)		1.28	0.71		12	19		6
		O(1)	C(1)		1.58	0.41		11	13		9
		C(1)	C(2)		0.86	1.05	[g]	34	16		15
		C(2)	C(3)		1.01	0.90	[h]	23	28		13
		C(3)	C(4)		0.94	1.00		26	22		12
		C(4)	C(5)		1.01	0.93	[i]	22	25		11
		C(5)	C(6)		1.01	0.98		27	15		8
	Single bond	C(6)	H(1)		1.08	0.93		37			9
C_3H_4 complete	τ bond	C(1)	C(2)		1.01	1.00		15	26		7
	Single bond	C(1)	H(1)		1.07	0.94		36			9
C_5H_4 complete	τ bond	C(1)	C(2)		0.99	1.00		15	27		8
		C(2)	C(3)		0.96	1.00		23	23		10
	Single bond	C(1)	H(1)		1.07	0.93		36			9
C_7H_4 complete	τ bond	C(1)	C(2)		0.98	1.01		16	26		8
		C(2)	C(3)		0.96	1.01		24	22		10
		C(3)	C(4)		0.98	0.97		23	24		11
	Single bond	C(1)	H(1)		1.08	0.93		36			9
C_2H_2 complete	τ bond	C(1)	C(2)		1.00	1.00		15	15		1
	Single bond	C(1)	H(1)		1.14	0.87		48			6
C_2H_4 complete	τ bond	C(1)	C(2)		1.01	1.01		18	18		6
	Single bond	C(1)	H(1)		1.06	0.96		36			9
Bent Structures[j]											
C_3 $\sigma-\pi$	Lone pair	C(1)			2.01			71			12
	σ bond	C(1)	C(2)		0.83	1.14		29	54		13
		C(1)	C(2)	C(3)	0.50	0.99	0.50	12	2	12	0
	π bond	C(1)	C(2)	C(3)	0.44	1.12	0.44	0	0	0	0
C_3 complete	Lone pair	C(1)			2.01			71			12
	τ bond	C(1)	C(2)		0.80	1.15		28	51		15
		C(1)	C(2)	C(3)	0.48	1.05	0.48	8	2	8	0
CO_2 $\sigma-\pi$	Lone pair	O(1)			2.02			68			17
	σ bond[k]	O(1)	C(1)		1.00	0.99		6	54		6
	[l]	O(1)	C(1)		1.61	0.38		32	2		13
	π bond	O(1)	C(1)		1.56	0.42		0	0		12
CO_2 complete	Lone pair	O(1)			2.00			64			18
	τ bond[k]	O(1)	C(1)		1.03	0.96		2	51		7
	[l]	O(1)	C(1)		1.58	0.40		21	3		12
OC_2H_2 complete	Lone pair	O(1)			1.99			71			20
	τ bond	O(1)	C(1)		1.29	0.71		13	18		6
		O(1)	C(1)		1.61	0.36		11	13		10
		C(1)	C(2)		1.07	0.94		47	0		10
		C(1)	C(2)		0.80	1.19		25	29		13
	Single bond	C(2)	H(1)		1.06	0.94		40			12

[a] From the Boys criterion unless noted, unique orbitals only. [b] Reference 33. [c] Population of 0.09 on C(1). [d] Population of 0.07 and 0.04 on C(1) and C(2), respectively. [e] Population of 0.03 on C(3). [f] Population of 0.05 on C(1). [g] Population of 0.05 on C(3). [h] Population of 0.05 on C(1). [i] Population of 0.04 on C(3). [j] Bends 55° for C_3 and CO_2; a 55° CH_2 out-of-plane bend for OC_2H_2. [k] Outside OCO triangle. [l] Inside OCO triangle.

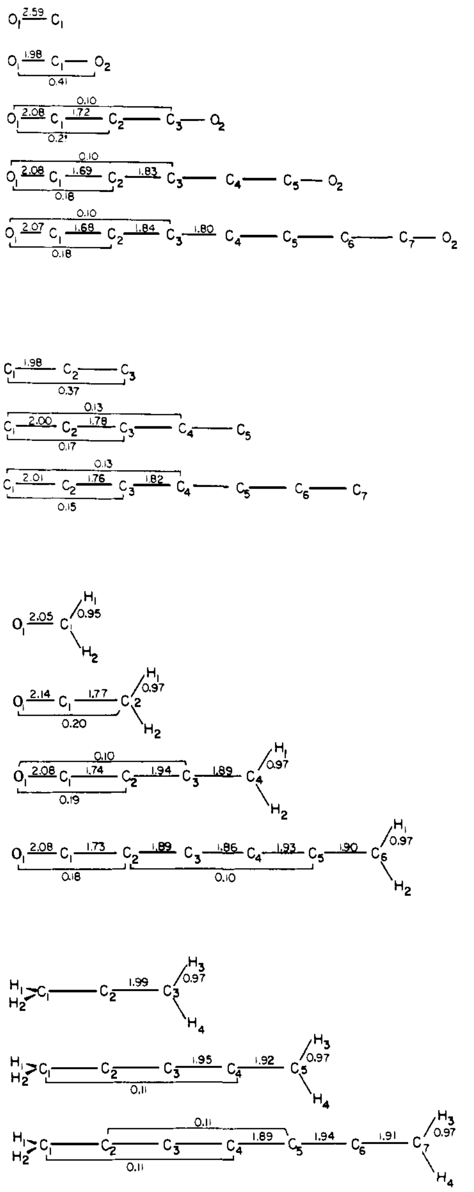


Figure 2. Bond indices. See ref 43. Values less than 0.10 valence units omitted. The C(1)C(3) bond index in H_2C_6O is 0.09 valence units.

two sets of triple bonds with respect to one another. This was previously found to be the case for CO_2,[35] where the opposing sets of fractional triple bonds are not required by the Boys criterion to be staggered or eclipsed with respect to one another. As measured by the second-derivative test, the H_4C_n molecules have the steepest localization surfaces.

For C_3 the two different localization criteria (Boys and Edmiston-Ruedenberg) produced almost identical results. Earlier work[35] has shown that in CO_2 the Edmiston-Ruedenberg (ER) and Boys localized structures differ. However, for a strongly bent configuration (∠OCO = 125°) the two criteria produce very similar results. For ketene the ER and Boys results also differ in their representation of the CO linkage (see below). These results suggest that for carbon suboxide, the ER and Boys criteria would yield essentially identical results for the CC bonds, but different results for the CO bonds.

The imposition of $\sigma-\pi$ separation on the localizations is a significant constraint. The $\sigma-\pi$ structures are found to lie on a saddle point on the complete localization surface in all cases examined: CO_2, C_3, and C_3O_2 (cf. ref 53). The $\sigma-\pi$ localizations produce very simple and easily understood LMO patterns.

Table II. Mulliken Atomic Populations on Center A in Two- and Three-Center LMO's[a]

Symbol	Two-center LMO's	Three-center LMO's
⇢ A	0.15-0.25	0.15-0.25
→ A	0.25-0.50	0.25-0.35
- - - A	0.50-0.75	0.35-0.50
— A	≥0.75	≥0.50

[a] For the complete localizations the line symbol is drawn from the approximate LMO centroid location to atom A. For the π localizations the line symbols are displaced above and below the centroid locations to avoid superimposing lines and obscuring the atomic symbol.

For the C_nO_2 and C_n molecules, both complete and $\sigma-\pi$ localizations produce three-center CCC bonds rather than cumulated double bonds such as those found in the localized results for $H_2C_nH_2$ and H_2C_nO. These are the first localized structures reported which have linear three-center bonds. Previously, three-center bonds have been reported for electron-deficient compounds, typically boron hydrides,[33] and aromatic hydrocarbons.[30,53b]

In the complete localizations for the C_nO_2 and C_n molecules, the three-center τ bonds show very low amounts of s character, approaching a $\sigma-\pi$ separation, a feature uncharacteristic of Boys localizations.[33b]

Examination of Table I and Figure 1 will reveal that several carbon atoms in the C_nO_2, C_n, and OC_nH_2 molecules are associated with more than four LMO's. These bonds employ nonorthogonal atomic orbital hybrids and are fractional to the carbons involved, as only four valence orbitals are available on each center in this minimum basis set treatment.[36] Fractional LMO's are symptomatic of an inherent or irremovable delocalization of electrons, the MO counterpart of resonance in the valence bond framework.[36] Fractional bonds are not as stabilizing per bond as are normal bonds, though they tend to reduce bond lengths nearly to values suggested by the number of fractional bonds.[36] The inclusion of higher order functions (e.g., 3d orbitals) would be expected to lower the energy of the fractionally bonded systems significantly, and such d functions would have nonnegligible populations.[36]

The $\sigma-\pi$ localizations for C_nO_2 and C_n molecules show that carbons with three-center bonds alternate with carbons having fractional bonds. For the three-center bonded carbons, the basic LMO pattern can be seen in C_3, where a π ungerade MO spans the three carbons and is centered on the central one. For the fractionally bonded carbons, CO_2 is the prototype: the π localization mixes the π gerade and π underade CMO's to produce fractional bonds to carbon.

Table III summarizes the energetics of bending for the molecules studied. Agreement with experiment is good for force constants in the normal or middle range. Agreement with experiment is only qualitative for unusually low or high values. The bending potentials for the C(1)C(2)C(3) angles generally are found to be very soft for C_n, C_nO_2, and H_2C_nO. The O(1)C(1)C(2) and C(2)C(3)C(4) angles, in contrast, are generally very stiff. The angles in the H_4C_n series are intermediate in stiffness, and the bending force constants may be considered to have normal values. In the PRDDO approximation all of the bending potentials have their energy minimum at 180°. We note that extended basis set results[7] produce both a more extreme charge distribution in C_3O_2 and a lower force constant for bending the central angle.

Table IV shows Mulliken atomic charges. For the C_nO_2 series the oxygen atom has a large negative charge, typically about −0.22 e. The adjacent carbon atom has an even larger positive charge, typically about 0.34 e. The next carbon is then negative with a charge similar to that of oxygen. The charges alternate down the length of the molecule, the magnitude of

Table III

Angle	Molecule	Charge[a]	$E = a_0\alpha^2 + a_1\alpha^4$ [b] $a_0 \times 10^3$	$a_1 \times 10^6$	Force constant,[c] kcal/mol deg$^2 \times 10^3$ Calcd	Obsd[d]
C(1)C(2)C(3)	C_3O_2	−0.26	4.8	−0.5	4.7	~0
	C_3	−0.39	4.9	−0.5	4.8	0.4
	C_5O_2	−0.22			5.3	
	H_2C_6O	−0.14			6.1	
	C_5	−0.27	6.2	−0.3	6.3	
	C_7	−0.26			6.5	
H(2)C(2)C(1)	H_2C_2O	−0.24 (−0.07)	6.5	−0.4	6.6	3.8
C(3)C(4)C(5)	C_7	−0.13			7.3	
C(1)C(2)C(3)	H_2C_4O	−0.16	7.7	−0.2	7.7	
C(3)C(4)C(5)	H_2C_6O	−0.09			8.1	
H(2)C(1)C(2)	C_5H_4	−0.15 (0.01)			8.5	
	C_3H_4	−0.17 (−0.01)	9.1	−0.1	9.0	9.2
H(2)C(4)C(3)	H_2C_4O	−0.19 (−0.02)			9.2	
C(2)C(3)C(4)	H_4C_5	−0.06	10.0	−0.1	10.1	
C(4)C(5)C(6)	H_2C_6O	0.05			10.5	
C(1)C(2)C(3)	H_4C_5	0.02	10.5	0.3	10.7	
C(2)C(3)C(4)	H_2C_6O	0.09			12.7	
C(1)C(2)C(3)	H_4C_3	0.03	12.4	0.5	12.7	13.1
C(2)C(3)C(4)	H_2C_4O	0.10	12.5	0.4	12.8	
H(2)C(1)O(1)	H_2CO	0.10 (0.22)	12.9	−0.5	12.9	13.6
O(1)C(1)C(2)	H_2C_2O	0.29	14.1	0.7	14.4	25.0
	H_2C_6O	0.30			14.6	
O(1)C(1)O(2)	CO_2	0.51	14.1	1.6	14.6	33.7
O(1)C(1)C(2)	H_2C_4O	0.30	15.3	0.4	15.4	
C(2)C(3)C(4)	C_7	0.22			16.4	
O(1)C(1)C(2)	C_5O_2	0.34			17.0	
C(2)C(3)C(4)	C_5	0.26	17.4	0.5	17.1	
O(1)C(1)C(2)	C_3O_2	0.36	18.0	0.2	17.9	28.9
C(2)C(3)C(4)	C_5O_2	0.19			18.1	

[a] At apex atom. Reference 44. For CH_2 out-of-plane bending, CH_2 group charge is shown in parentheses. [b] E in kcal/mol, $\alpha = 180 - \angle$, determined for $\alpha = 0, 5, 10, 15, 20, 25, 30$, and 35°. [c] Determined for $\alpha = 0, 5, 10, 15$, and 20° except for C_7, H_2C_6O, and C_5O_2, where $\alpha = 0, 10$, and 20°. [d] Reference 62b.

Table IV. Atomic Charges

Molecule	O(1)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	H
CO	−0.23	0.23						
CO_2	−0.26	0.51						
C_3O_2	−0.23	0.36	−0.26					
C_5O_2	−0.22	0.34	−0.22	0.19				
C_7O_2	−0.22	0.34	−0.20	0.17	−0.17			
C_3[a]		0.19	−0.39					
C_5		0.14	−0.27	0.26				
C_7		0.11	−0.26	0.22	−0.13			
H_2CO	−0.22	0.10						0.06
H_2C_2O[b]	−0.22	0.29	−0.24					0.09
H_2C_4O	−0.22	0.30	−0.16	0.10	−0.19			0.09
H_2C_6O	−0.21	0.30	−0.14	0.09	−0.09	0.05	−0.17	0.09
C_3H_4		−0.17	0.03					0.08
C_5H_4		−0.15	0.02	−0.06				0.08
C_7H_4		−0.15	0.02	−0.04	0.00			0.08

[a] Ab initio values are 0.17 and −0.35 for C(1) and C(2), respectively. [b] Ab initio values are −0.20, 0.28, −0.25, and 0.09 for O(1), C(1), C(2), and H, respectively.

the charges being smaller toward the middle of the larger homologues. This is in qualitative agreement with earlier studies of C_3O_2,[4,12,13,17] though the largest basis set results[7] show that the charge distribution to be even more extreme (cf. ref 4, 15, and 19).

For the C_n series the end carbons are positive and the adjacent carbons are even more negative. The remaining charges alternate down the length of the molecule, again with reduced charges for the central regions of the larger homologues. The greater charges are found in the smaller homologues. The PRDDO atomic charges for C_3 agree closely with ab initio values (Table IV and ref 22).

For H_2C_nO the charge pattern is similar to that for C_nO_2, with charges becoming smaller toward the hydrogenic end of the molecule. The final CH_2 group charge is almost zero, with the negative charge on carbon being roughly balanced by the positive charges on the hydrogens. However, there are exceptions to this last generalization. For formaldehyde the CH_2 group charge is positive (0.22 e). For ketene it is negative (−0.07 e). For H_2C_4O the negative charge is very small (−0.02

Table V. Valencies[a]

Molecule	O(1)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	H
CO	2.59	2.59						
CO_2	2.39	3.96						
C_3O_2	2.48	3.94	3.86					
C_5O_2	2.49	3.94	3.91	3.95				
C_7O_2	2.49	3.95	3.92	3.96	3.96			
C_3		2.34	3.95					
C_5		2.43	3.96	3.91				
C_7		2.45	3.96	3.94	3.97			
H_2CO	2.13	3.96						1.00
H_2C_2O	2.38	3.92	3.90					1.00
H_2C_4O	2.42	3.95	3.94	3.97	3.98			1.00
H_2C_6O	2.43	3.95	3.94	3.98	3.99	3.99	3.99	1.00
H_4C_3		3.99	3.99					1.00
H_4C_5		3.99	4.00	4.00				1.00
H_4C_7		3.99	4.00	4.00	4.00			1.00

[a] Reference 43.

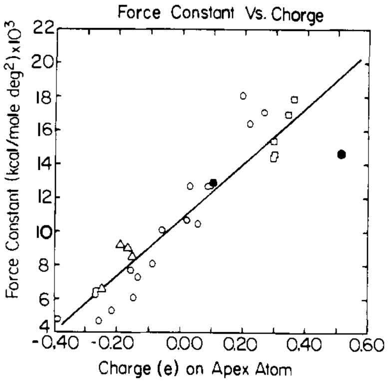


Figure 3. PRDDO force constants × 10^3 (in kcal/mol deg^2) vs. Mulliken charge at apex atom in electrons: ○ ∠CCC; □ ∠CCO; △ ∠(H_2)CC; ■ ∠(H)$_2$CO; ● ∠OCO. A linear least-squares interpolation is shown.

Table VI. PRDDO Energies

Molecule	SCF energy, au
CO	−112.3404
CO_2	−186.9306
C_3O_2	−262.4624
C_5O_2	−337.9959
C_7O_2	−413.5347
C_3	−113.1124[a]
C_5	−188.6470
C_7	−264.1868
H_2CO	−113.4952
H_2C_2O	−151.2743[b]
H_2C_4O	−226.8057
H_2C_6O	−302.3464
H_4C_2	−77.8883
H_4C_3	−115.6579
H_4C_5	−191.1957
H_4C_7	−266.7395
H_2C_2	−76.5774

[a] Ab initio value is −113.0555. [b] Ab initio value is −151.2298.

e), and for H_2C_6O the group charge is very slightly positive (0.01 e).

For the hydrocumulenes, the charge distribution is not far from electroneutrality. The CH_2 group charges are −0.01, 0.01, and 0.02 e in C_3H_4, C_5H_4, and C_7H_4 respectively.

Examination of the σ-π localizations as well as orbital populations shows that the significant deviations from electroneutrality are largely a π-orbital phenomenon which is in some cases mitigated by the polarity of the σ system.[55]

Table III and Figure 3 show the relationship between the bending force constant and the gross atomic charge of the atom at the apex of the angle. Table V shows atomic valencies. Figure 2 shows bond indices. Low valencies are found for both high and low bending force constants, while valencies of nearly four are associated with normal bending force constants. The SCF energies of the molecules studied appear in Table VI.[56]

For C_3 the ab initio and PRDDO eigenvalues agree closely.[57,58] However, they differ in their ordering of the $1\pi_u$ and $3\sigma_u$ orbitals, which are quite close in energy. The PRDDO calculation has the $3\sigma_u$ orbital as the HOMO, while the ab initio calculation and ref 23 and 24 show the $1\pi_u$ orbital to be the HOMO. For ketene the PRDDO eigenvalues are also quite close to the ab initio values, and no inversions in ordering are found.[57,59] For carbon suboxide the ordering of the PRDDO orbital energies is the same as that reported in ref 7.[57]

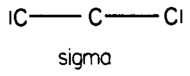
Atoms associated with soft bending potentials not only have appreciable negative charges, but also are near the centroids of three-center bonds. The centroid of the π HOMO, the three-center π LMO, and the three-center τ LMO in the complete localization all reside at or near the central carbon in C_3 and C_3O_2, for example. Atoms associated with hard bending potentials not only have positive charges, but also are fractionally bonded, as in CO_2 or the end carbon atoms in C_3O_2. As previously proposed[6,12] the oxycumulene carbons do show regular alternations in their electronic structure.

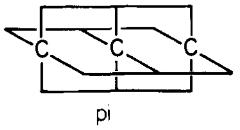
Discussion

C_3. The LMO's for the C_3 molecule include three inner shells[60] and two carbon lone pairs. In addition, both the σ-π and complete localizations using both the ER and Boys criteria show that the carbons are linked by two three-center and two two-center LMO's. The CC bond index is 1.98. The valency of the end carbon is only 2.34, lower than for other carbons with lone pairs in C_5 (2.43), C_7 (2.45), or CO (2.59). The three-center π LMO and the three-center LMO from the complete localization are shown in Figures 4a and b, respectively. A close examination of the LMO centroids in C_3 reveals that in the complete Boys localization for the linear configuration, the lone pair orbitals do not lie exactly along the internuclear axis, but are slightly displaced to one side (away from the three-center bonds) in the plane of the two-center bonds.

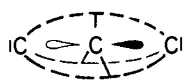
A recurrent pattern in the oxycumulene and carbon molecule localizations is the presence of three-center CCC bonds rather than cumulated double bonds. Examination of the LMO's for C_3, the simplest case, reveals how the three-center

LMO's are obtained. We note that normal localized cumulated double bonds (as in allene) would not reflect the cylindrical symmetry of the molecule. In typical LMO structures cylindrical symmetry in multiple bonding is represented through localized triple bonds (three τ bonds or a σ and two π bonds) as in H_2C_2 or CO. Alternatively, cylindrical symmetry may be represented through the delocalization of electrons. The σ–π localized structure for C_3 clearly reflects the cylindrical symmetry of the molecule. The three inner shells are essentially the sum and difference of the $1\sigma_g$ and $1\sigma_u$ CMO's and the $2\sigma_g$ CMO. The CC σ bonds are essentially the sum and difference of the $3\sigma_g$ and $2\sigma_u$ CMO's, and the lone pairs are essentially the sum and difference of the $4\sigma_g$ and $3\sigma_u$ CMO's. Some additional mixing of the σ MO's improves the localization. The π LMO's are simply the π CMO's. Mixing the two π MO's merely rotates them about the molecular axis. Mixing the CC σ and CCC π LMO's produces the complete localization. The extent and manner of this mixing is determined by the localization criterion, but is nearly the same for both criteria used. The resulting LMO structure has cylindrical symmetry. Any apparent gaps or pockets which might be implied by the sketch are filled in by the sum of the LMO densities. The two three-center τ LMO's are obtained from mixing the $3\sigma_g$ CMO with the π MO's. The two-center π LMO's are obtained by mixing the π MO's with both the $3\sigma_g$ and $2\sigma_u$ CMO's, i.e., the two CC σ LMO's less some portion of the $3\sigma_g$ CMO.

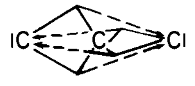


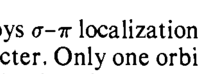


Of course, other ways of localizing the MO's are possible. Any unitary transformation applied to the occupied CMO's does not change the Slater determinant and so is allowable. However, other transformations do not satisfy the localization criteria used or necessarily make chemical sense. Among the more plausible alternatives to the above localization are the following. First, mixing the two π MO's with the $3\sigma_g$ CMO (avoiding any admixture of the $2\sigma_u$ CMO) produces a structure which places four valence LMO centroids in the plane perpendicular to the molecular axis containing the central atom.



Second, mixing the π_x MO with one CC σ MO and then mixing the π_y MO with the other CC σ LMO, produces a structure related to the cumulated double bonds of allene with an important difference: the CC τ bonds produced must have significant tails to the third carbon. Third, mixing both π MO's with one CC LMO only produces a structure with three delocalized τ bonds on one side of the central carbon and one LMO on the other side of the molecule. In this structure the LMO centroids are arranged with local C_{3v} symmetry around the central carbon (cf. C_5O_2 below).





On bending, the Boys σ–π localization (Figure 1z) assumes a much altered character. Only one orbital retains the π designation (the b_2 CMO). The other π_u orbital becomes an a_1 (σ) orbital. The σ_g and σ_u CMO's become a_1 and b_1 CMO's, respectively. The σ localization now shows bent bonds with centroids which lie outside the carbon triangle and a three-center bond with a centroid inside the carbon triangle. The π localization shows a three-center bond of the expected form. The complete localization (Figure 1y) shows that the two three-center bonds are mixed to form three-center τ bonds above and below the plane of the molecule while the two-center τ bonds remain in the molecular plane. As in the linear form, the carbon lone pairs do not lie exactly on the CC vector.

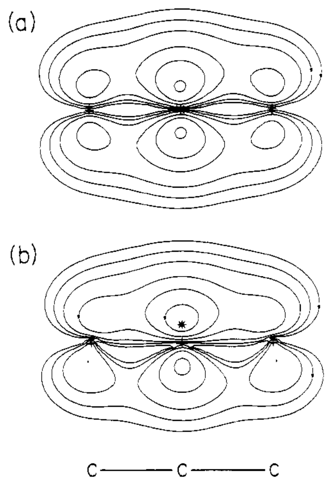


Figure 4. Three-center LMO's in C_3: (a) σ–π localization; (b) complete localization. Contour levels are 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 e/au^3 with two electrons in each LMO. Crosses mark atomic centers, asterisks mark LMO centroids.

CO. The LMO's for carbon monoxide (Figure 1a) display a carbon lone pair, similar to that found in C_3, an oxygen lone pair, and a polar triple bond (cf. ref 42b). In the σ–π localization (Figure 1b) the σ bond is distinctly polar, though less so than the π bonds. The complete localization produces a set of polar τ bonds. The CO bond index of 2.59 shows that a polar triple bond is an appropriate representation of the electronic structure. We note that it would be possible to localize CO with a double bond and two oxygen lone pairs by mixing the two-center σ LMO with the π_x MO and the oxygen lone pair with the π_y MO. The two lone pairs thus produced, however, would necessarily have delocalized tails to carbon (cf. the ER localization of CO_2[35]). Of course, intermediate amounts of LMO mixing can produce a compromise between a double and a triple bond representation (see ketene below). We also note that none of the carbon monoxide LMO's are fractional.

CO_2. The Boys LMO's for carbon dioxide,[35] in contrast, are fractional[36] to carbon with one lone pair on each oxygen (as in carbon monoxide) and polar triple bonds connecting each oxygen to carbon (Figure 1c). The OC bond index of 1.98 indicates that the fractional triple bonds resemble double bonds in strength. The σ–π localization (Figure 1d) shows that the σ bonds are less polar than in CO. Table IV shows that the atomic charge distribution in CO_2 is the most extreme of all the molecules studied: the oxygen is the most negative and the carbon the most positive. The oxygen valence (2.39) is below that found in CO (2.59) and in C_3O_2 (2.48), comparable to the value in H_2C_2O (2.38) and higher than in the case of H_2CO (2.13). The 1,3-oxygen-oxygen interaction (bond index 0.41, overlap population −0.02) is more important than any 1,3-interaction in the other cumulenes studied.

For bent CO_2 the π_g CMO's become a_2 (π) and b_1 (σ) MO's. In the complete localization (Figure 1w) the LMO's are arranged as follows. The two-center LMO's lie in the plane of the molecule, but are bent so that their centroids lie outside of the OCO triangle. Four two-center LMO's lie within the OCO triangle, paired on each side of the carbon above and below the

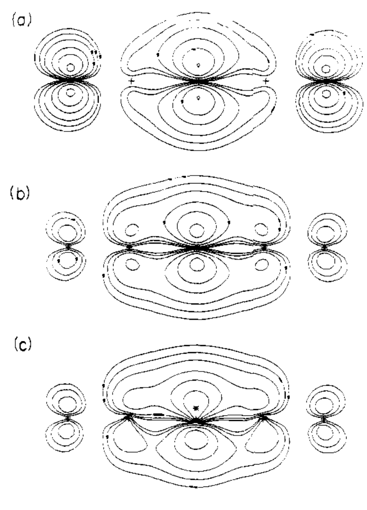


Figure 5. Three-center LMO's in C_3O_2: (a) π CMO; (b) σ–π localization; (c) complete localization. Same markings and contour levels as in Figure 4.

plane of the molecule. The oxygen lone pairs lie in the molecular plane, but are not aligned with the OC vectors. In the σ–π framework there are four (fractional) bent CO bonds which lie in the plane of the molecule. Two of these (those inside the OCO triangle) are very polar toward oxygen (1.61 e on 0). There are also two fractional CO π bonds and two oxygen lone pairs.

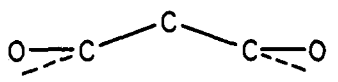
The complete and σ–π ER LMO's for the linear configuration of CO_2 have previously been reported.[35] Each carbon has two delocalized lone pairs on each oxygen in addition to cumulated CO double bonds which define perpendicular planes. The complete and σ–π localizations for a strongly bent

configuration (∠OCO = 125°) of CO_2 using the ER criterion are very similar to the Boys results.

C_3O_2. The LMO's for carbon suboxide are depicted in Figures 1e and f. Each oxygen has a lone pair, much as in CO and CO_2, and is connected to carbon by fractional polar triple bonds as in CO_2 (Boys localization). The three carbons are linked in both the σ–π and complete localizations by two two-center and two three-center bonds as in C_3. Electron density maps of the π_g CMO, the three-center π LMO, and the three-center τ LMO from the σ–π localization are shown in Figures 5a, b, and c, respectively. Bond indices for C_3O_2 indicate that the CO bond is intermediate in strength between carbon monoxide and carbon dioxide CO bonds. The CO bond index (2.08) is greater than two, while the CC bond index is slightly less than two (1.72). The 1,3- and 1,4-interactions are also important, indicative of delocalized bonding. The middle carbon valency is very low, only 3.86.

The σ–π localization and the orbital populations both reveal that the σ orbital charge distribution opposes to some extent the π orbital charge distribution.[55] This was not found to be the case for CO or CO_2. The π LMO's are very polar, the σ LMO's much less so.

Both Christoffersen et al.[6] and Seip et al.[7] found that when the CCC angle is nonlinear, a zigzag conformation for carbon suboxide is most stable. A hint of this zigzag structure is found in the LMO centroid locations for the complete localization.



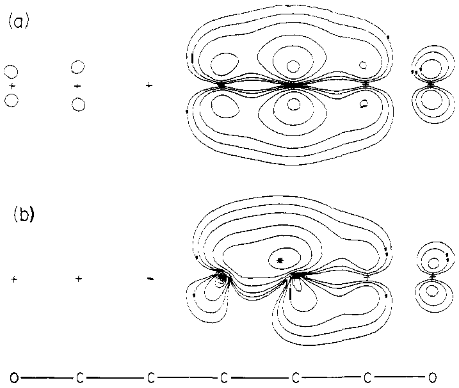


Figure 6. Three-center LMO's in C_5O_2: (a) σ–π localization; (b) complete localization. Markings and contour levels as in Figure 4.

The plane of the three centroids for the CO τ bonds is slightly tilted so as to be not quite perpendicular to the molecular axis. The oxygen lone pairs are also tilted off the internuclear axis and lie in the plane of the two-center bonds.

C_5O_2. The existence of C_5O_2 and its structure have not been established. With a geometry analogous to that used for C_3O_2, localized orbitals as shown in Figures 1g and h are obtained. There are four important differences between the C_5O_2 and C_3O_2 localizations. First, the three-center bonds (in both the complete and σ–π localizations) are now centered near carbons 2 and 4, precisely those atoms associated with soft bending potentials (Table III) and large negative charges (Table IV). Second, seven LMO's each are associated with carbons 1 and 5 in the complete localization (Figure 1g), an unusually large number, indicating extreme fractionality in the LMO's. Third, the CC bond indices fall significantly below two (1.69 for C(1)C(2)) despite the large numbers of LMO's joining the carbon atoms. Fourth, the central carbon atom adopts a previously unobserved LMO pattern. This atom has an unusually high PRDDO bending force constant (18.1×10^3 kcal/mol deg^2), a valency relatively close to four (3.95), and a positive charge (0.96 e). Figures 6a, b, and c show the π CMO, the three-center LMO in the σ–π localization, and the three-center LMO in the complete localization.

C_7O_2. The assumed geometry for C_7O_2 leads to an LMO structure in which carbons 1 and 7 resemble carbons 1 and 5 of C_5O_2, carbons 2 and 6 resemble carbon 2 of C_5O_2, and carbon 4 resembles carbon 2 of C_3O_2. On the basis of the atomic charges and the LMO pattern, carbons 2, 4, and 6 should have soft bending potentials. This is in accord with previous predictions.[6,12] The bond indices, considerably less than two (1.68–1.34) for the CC bonds, and only slightly greater than two (2.07) for the CO bonds, resemble those for C_5O_2.

C_n and C_nO_2 LMO Patterns. The C_n localizations resemble the C_nO_2 localizations with CO bonds replaced by lone pairs. For the larger C_nO_2 and C_n homologues, the π LMO centroids are spaced approximately equally along the length of the molecules, consistent with the Boys criteria of maximum separation of orbital centroids. We note that the maxima and nodes of the π CMO's tend to fall on or nearly on carbon atoms for the central regions of the molecules. The carbons closest to the π LMO centroids have the most negative charges and the lowest bending force constants. The localized σ systems are very regular with centroids near the midpoints between the pairs of atoms.

Figure 7 summarizes the two different ways the σ and π orbitals mix in the C_nO_2 and C_n molecules. In Figure 7a the π centroid is located exactly on carbon 2. The complete localization shows the centroids are located about carbon 2 with local D_{2d} symmetry. This pattern is seen at carbon 2 in C_3O_2 and C_3 and at carbon 4 in C_7O_2 and C_7. In Figure 7b the π

centroid is displaced slightly toward C(3). In the complete localization the centroids about carbon 2 show local C_{3v} symmetry, with the three-fold axis coincident with the molecular axis. This pattern is seen for C(2) and C(4) in C_5O_2 and C(2) and C(6) in C_7O_2 and C_7. Of course, the total electron density still has cylindrical symmetry in all cases.

The case of C_5 at first seems anomalous in that it does not resemble C_5O_2 more closely for the complete localizations. We note that the π LMO centroid is only 0.11 au distant from carbon 2 in C_5. The distance in C_5O_2 is 0.18 au; in C_7 it is 0.17 au. In C_5 there are slight distortions of the LMO centroids from local D_{2d} symmetry. Moreover, the C(2)C(3) two-center τ LMO is 15% delocalized with a population of 0.09 e on carbon 1. Thus, the overall result is intermediate between the two idealized cases in Figures 7a and b. The variety of ways in which σ and π LMO's mix in the complete localization makes the prediction of LMO patterns a nontrivial matter.

C_nH_4. The hydrocumulenes have a much simpler LMO pattern than the oxycumulenes and carbon molecules. Each C_nH_4 molecule has cumulated CC double bonds and single CH bonds (Figure 1t-v). The LMO's are much less delocalized than in the oxycumulenes. As both the percent delocalization[33] and the populations in Table I indicate, the bonds are slightly more delocalized in C_5H_4 and C_7H_4 than in C_3H_4. The 1,4-interactions, as measured by the bond indices, are important for the higher members of the series. The Mulliken charges throughout the series are quite modest; valencies differ very little from four and one for carbon and hydrogen, respectively, and the bending force constants are in the normal range. In short, allene and its homologues have normal cumulated double bonds. We note that the maxima and the nodes for the hydrocumulene π CMO's fall between the carbon atoms, and the π LMO centroids consequently lie between the carbon atoms.

H_2C_nO. The LMO's for formaldehyde using the ER criterion have been reported previously.[53a] The results using the Boys criterion (Figure 1p) are very similar. In both cases oxygen has two lone pairs, carbon and oxygen are linked by a bent double bond, and single bonds join the carbon with each hydrogen.

The LMO's for ketene (Figure 1q) resemble the allene LMO's for the hydrogenic end of the molecule, but have a different pattern for the CO linkage. In the complete Boys localization for ketene, the oxygen atom has only one lone pair. This lone pair does not lie along the internuclear axis, but lies to one side of the molecular plane. The lone pair is noticeably more delocalized (20%) than is the lone pair on carbon monoxide (16% delocalization), though the percent delocalization is comparable to that found for lone pairs in C_nO_2. The oxygen and carbon are connected by three τ bonds. Two of these bonds are equivalent, distinctly polar (1.24 e on O), and lie to one side of the molecular plane (the same side as the lone pair). One of the bent bonds is unique, extremely polar (1.72 e on O), and lies to the other side of the molecular plane. Thus the LMO centroids about oxygen form a distorted tetrahedron as in formaldehyde and carbon suboxide, but the tetrahedron has been rotated so that neither the threefold nor the twofold axis is coincident with the molecular axis. The CO bond in ketene is thus a compromise between a double bond and a triple bond. The CO bond index is 2.14, significantly greater than two. The two carbons in ketene are joined by a pair of very nearly equivalent τ bonds. The CC bond index is 1.77, significantly less than two. The Boys LMO pattern for ketene recurs in the higher homologues. Cumulated CC double bonds are found in OC_4H_2 and OC_6H_2. These bonds are more delocalized than those in the corresponding hydrocumulenes (see Table I).

The (complete) ER localization for ketene represents the CO bonding in a different fashion. The carbon and oxygen are joined by two equivalent τ bonds which lie in the plane of the molecule. The oxygen now has *two* delocalized lone pairs. These lone pairs are 18% delocalized and have 0.07 e population on the adjacent carbon. By way of comparison, the Boys localized formaldehyde lone pairs are 12% delocalized[61] with 0.01 e on carbon, and the ER localized carbon dioxide ions pairs are 25% delocalized with 0.18 e on carbon.[35]

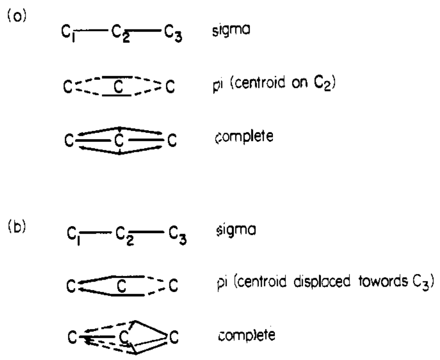
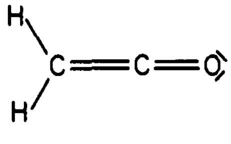


Figure 7. LMO patterns in C_n and C_nO_2 molecules: (a) π LMO centered on C(2); (b) π LMO not centered on C(2). See Table II for notation.

For ketene the following has been presented to explain the ease of out-of-plane CH_2 bending.[62] The two principal valence bond structures are I and II. In II the CH_2 group will tend to bend out of the plane. The LMO structure for ketene supports this explanation and is a compromise between I and II, with the CO bond picking up some triple bond character as reflected in the bond index (2.14) and in both the Boys and ER localizations. The gross charges on C(1), C(1), and C(2) are −0.22, 0.29, and −0.24 e, respectively. The charge on oxygen does not vary appreciably from that found in formaldehyde.



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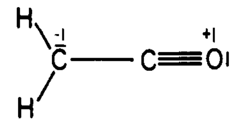
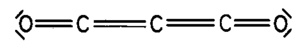


II

Upon CH_2 out-of-plane bending, the Boys LMO structure begins to resemble II more than I: the oxygen lone pair more closely approaches coincidence with the CO axis, the CO τ bonds become more alike, and the CC τ bonds become noticeably nonequivalent.

CCC Bending. The LMO results presented above allow previous explanations for the low bending force constants in oxycumulenes to be reformulated in a different language. In valence bond terms carbon suboxide has been represented as a hybrid of structures III-IX.[13] It is generally agreed that III



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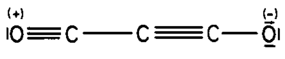

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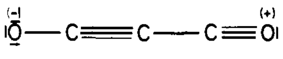

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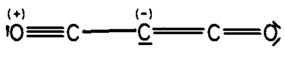

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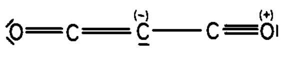

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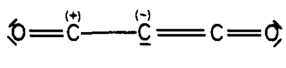

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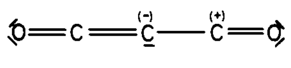


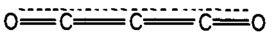
IX

Table VII. Energy Analysis for C_3O_2 Bending[a,b]

Method	PRDDO		Method of molecular fragments[c]	
∠CCC	180	125[d]	180	125[d]
Nuclear attraction energy	−862.2440	−6.6958	−763.2481	−6.8140
Electron repulsion energy	216.0246	3.1224	204.4956	3.2343
Nuclear repulsion energy	121.8011	3.3532	121.8011	3.3532
Kinetic energy	261.9559	0.2407	212.0581	0.2241
Total energy	−262.4624	0.0205	−224.8934	−0.0023

[a] Energies in atomic units. [b] Geometries taken from ref 6. [c] "Non-split" basis, ref 6. [d] Relative to 180° form: ∠CCO = 180°.

is the principal structure, though VI and VII, and to a lesser extent VIII and IX, contribute sufficiently to the overall structure to reduce the bending force constant at the central carbon to nearly zero. Structure X was proposed by Pauling[1]



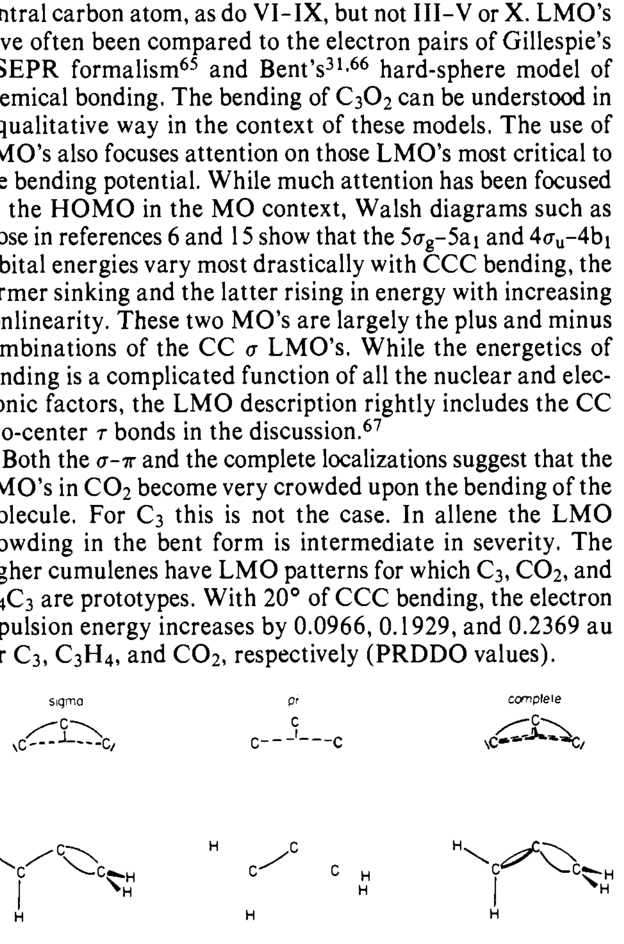
X

as a convenient representation of the delocalized nature of the electronic structure.

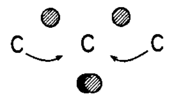
In the MO framework, the symmetry of the highest occupied molecular orbital has been the focus of attention.[63] In carbon suboxide the HOMO's are the degenerate π_u orbitals. The Walsh rules[64] are then invoked to explain the flexible nature of the CCC angle.

The congruence of the Walsh rules and LMO dispositions has been noted by Thompson.[34] The LMO representation of C_3O_2 (Figure 2e and f) suggests the unique nature of the central carbon atom, as do VI-IX, but not III-V or X. LMO's have often been compared to the electron pairs of Gillespie's VSEPR formalism[65] and Bent's[31,66] hard-sphere model of chemical bonding. The bending of C_3O_2 can be understood in a qualitative way in the context of these models. The use of LMO's also focuses attention on those LMO's most critical to the bending potential. While much attention has been focused on the HOMO in the MO context, Walsh diagrams such as those in references 6 and 15 show that the $5\sigma_g$–$5a_1$ and $4\sigma_u$–$4b_1$ orbital energies vary most drastically with CCC bending, the former sinking and the latter rising in energy with increasing nonlinearity. These two MO's are largely the plus and minus combinations of the CC σ LMO's. While the energetics of bending is a complicated function of all the nuclear and electronic factors, the LMO description rightly includes the CC two-center τ bonds in the discussion.[67]

Both the σ–π and the complete localizations suggest that the LMO's in CO_2 become very crowded upon the bending of the molecule. For C_3 this is not the case. In allene the LMO crowding in the bent form is intermediate in severity. The higher cumulenes have LMO patterns for which C_3, CO_2, and H_4C_3 are prototypes. With 20° of CCC bending, the electron repulsion energy increases by 0.0966, 0.1929, and 0.2369 au for C_3, C_3H_4, and CO_2, respectively (PRDDO values).



The use of hard spheres to represent LMO's suggests the following analysis of the bending of C_3 and C_3O_2. The packing of hard spheres centered on the LMO centroid positions in C_3 produces the existence of what Bent has termed "electride ion pockets".[66a,68] On bending, the end carbons move into these pockets, i.e., into the faces of the distorted tetrahedron formed by the four LMO centroids associated with the central carbon. We recognize, of course, that the sum of the LMO densities gives a cylindrical electron density in the linear form of C_3 and C_3O_2; i.e., the electride ion pockets are filled by the delocalization of electrons. Nevertheless, the existence of a chemically reasonable electride ion packing scheme (LMO pattern) for the bent form should alert us to the possibility that the nonlinear configuration might be stable or that the bending force constant might be low.



The hard-sphere model suggests that the bent form of carbon suboxide should have greater nuclear-electron attraction at the cost of greater nuclear-nuclear repulsion and slightly greater electron-electron repulsion as the carbon nuclei move into the "electride ion pockets". Examination of Table VII shows that in the PRDDO treatment the nuclear attraction term does indeed favor the bent form, though this is partially offset by the nuclear repulsion and electron repulsion terms. The kinetic energy, which plays no role in the simple model, favors the linear configuration. The nuclear attraction term favors the bent form even more strongly in the molecular fragments treatment[6] than was the case in the PRDDO treatment.

Summary

The cumulenes investigated have diverse LMO patterns. Allene and its hydrocumulene homologues can be described reasonably well by localized cumulated double bonds. Carbon suboxide, the C_3 molecule, and their homologues in their localized structures have carbons at the middle of three-center CCC bonds alternating with fractionally bonded carbons. Their electronic structure is perhaps most easily understood in a σ–π localization. Ketene and its homologues display cumulated CC bonds and CO bonds intermediate between a double and a triple bond.

Both CCC bending and out-of-plane CH_2 bending force constants are strongly related to atomic charges for all the molecules studied. In the oxycumulenes and the C_n molecules, carbons near three-center bond centroids have appreciable negative charges and low bending force constants. The carbons associated with fractional bonds as in CO_2 have positive charges and high bending force constants.

A word of caution is in order. The definitive theoretical study of carbon suboxide and ts relatives has not yet arrived. Seip et al.[7] suggest that a large, well balanced basis set with two Gaussian d orbitals might be required to give satisfactory agreement with experiment for the bending of C_3O_2. The prediction of LMO patterns is difficult for molecules with delocalized electrons, especially so since the LMO's can be arranged to reflect subtle changes in electron density. The effect on basis set expansion (which is critical in quantitative reproduction of bending forces constants in oxycumulenes) on the LMO description remains to be explored. Finally, localized molecular orbitals are not observables, but are mathematical constructs. Other localized bond approaches, such as Goddard's GVB method,[69] may produce structures which do not resemble closely the LMO results for cumulenes. However, it is hoped that insights may be gathered from comparatively simple treatments for a series of related molecules which will make the electronic structure of cumulenes more understandable.

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(56) SCF convergence was considered achieved when the rms charge in the density matrix was 0.00001 e. For C_5O_2, C_7, and C_7O_2 values of 0.000 02, 0.000 07, and 0.000 31, respectively, were accepted after 45 iterations.
(57) Eigenvalues are available in the Ph.D. thesis of L. D. Brown.
(58) The rms difference between the PRDDO and ab initio eigenvalues is 0.0128 au.
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