Ab Initio Calculations on Large Molecules Using Molecular Fragments. Cumulenes and Related Molecules[1a]

Ludwik J. Weimann and Ralph E. Christoffersen*[1b]

Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66044. Received September 28, 1972

Abstract: *Ab initio* SCF calculations are carried out on a series of hydrocumulenes, oxycumulenes, and related molecules using the molecular fragment approach. The molecules studied include formaldehyde, carbon dioxide, allene, ketene, ketenimine, acetylene, carbon suboxide, and C_5O_2. Both geometric and electronic structure are investigated and related to available observed physical and chemical behavior of the molecules, and observations regarding the electronic and geometric structure of oxycumulenes in general are made.

Rationalization of the observed physical and chemical characteristics of organic cumulenes in terms of molecular structure theory has been beset by various difficulties. These difficulties arise in part owing to a lack of data on molecules in this series but are also due to a lack of a unified theoretical treatment that is consistent with available data on the various members of these series. However, the recent development[2-9] of an *ab initio* technique that can be used to investigate large molecules in a practical manner allows a systematic investigation of several of the important members of this series to be carried out.

In particular, several molecules of the hydrocarbon cumulene series $H_2C{=}(C)_n{=}CH_2$ and the oxycarbon cumulene series $O{=}C{=}(C)_m{=}C{=}O$ are investigated. These studies, described in the following sections, include several aspects of the geometric and electronic structure of C_2H_2, C_2H_4, C_3H_4, H_2CO, CO_2, C_3O_2, C_5O_2, $H_2C{=}C{=}O$, and $H_2C{=}C{=}NH$. Comparisons with both experimental and other theoretical investigations are made when possible, and the use of basis sets of the same relative merit allows a unified discussion of the properties of these molecules. Finally, predictions are made concerning the electronic and geometric structure of the experimentally uncharacterized C_5O_2 and ketenimine molecules.

Procedure

The details of the procedure for treating molecular fragments and forming a molecule by suitable combination of them have been described previously,[2,5] and only a summary of the important features is included here. The basis functions used in these studies are normalized, floating spherical Gaussians (FSGO) defined as

$$G_i(\mathbf{r}) = (2\pi/\rho_i^2)^{3/4} \exp\{-(\mathbf{r} - \mathbf{R}_i)^2/\rho_i^2\} \tag{1}$$

where ρ_i determines the size of the FSGO, and $\mathbf{R}_i$ is the location of the FSGO, relative to some arbitrary origin. For π-type orbitals, a normalized linear combination of two FSGO is employed, *i.e.*

$$G_\pi = [2(1 - \Delta_{ud})]^{-1/2}(G_u - G_d) \tag{2}$$

where G_u and G_d are FSGO that are symmetrically placed above and below the central atom on a line perpendicular to the plane of atoms, and Δ_{ud} is the overlap between G_u and G_d. The nonlinear parameters in the various molecular fragments are determined by means of investigations of appropriate molecular fragments, using a slight modification of an approach suggested by Frost and coworkers.[10-12]

After investigation of the molecular fragments has been completed, larger molecules are formed by suitable combinations of various molecular fragments and associated FSGO. Molecular orbitals (MO) are then obtained *via* the usual Roothaan-Hall SCF procedure,[13,14] *i.e.*

$$\varphi_i = \sum_{A=1}^{Q} \sum_{j=1}^{N_A} c_{ji}{}^A G_j{}^A \tag{3}$$

where the sums are taken over all fragments (Q) and all orbitals within each fragment (N_A). Throughout the fragment and SCF calculations double precision arithmetic has been employed, using a Honeywell 635 computer. Also, convergence of the SCF procedure was assumed when

$$\left|\frac{P_{jk}{}^{(i+1)} - P_{jk}{}^{(i)}}{P_{jk}{}^{(i)}}\right| \leq 10^{-5} \tag{4}$$

for all j and k, where $P_{jk}{}^{(i)}$ is an element of the charge and bond order matrix at the end of the ith SCF iteration, and

$$(\mathbf{P})_{jk} = 2\sum_{l}^{\text{occ}} c_{jl}c_{kl} \tag{5}$$

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[2] (a) R. E. Christoffersen and G. M. Maggiora, *Chem. Phys. Lett.*, **3**, 419 (1969); (b) R. E. Christoffersen, D. W. Genson, and G. M. Maggiora, *J. Chem. Phys.*, **54**, 239 (1971).

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Table I. Molecular Fragments of Interest

Molecular fragment	Common use	"Non-split" description: FSGO type	"Non-split" description: Orbital radius, ρ	"Non-split" description: Distance[a]	"Split-1s" description: FSGO type	"Split-1s" description: Orbital radius, ρ	"Split-1s" description: Distance[a]
CH_4 (T_d)	CH bonds	C-1s[d]	0.32784375	0.0	C-1s[d]	0.38789062	0.0
(R_{CH} = 2.05982176)		CH	1.67251562	1.23379402		(2.45705200)[b]	
						0.14716491	0.0
						(3.32478347)[b]	
					CH	1.67251562	1.23379402
$\cdot CH_3$ (sp^2)	Carbon multiple bonds	C-1s	0.32682735	0.0	C-1s	0.38704345	0.0
(R_{CH} = 1.78562447)		CH	1.51399487	1.13093139		(2.46348616)[b]	
		π[c]	1.80394801	±0.1		0.14726379	0.0
						(3.32424282)[b]	
					CH	1.51405884	1.12942291
					π[c]	1.78885620	±0.1
$\cdot OH$ (sp^2)	Oxygen multiple bonds	O-1s	0.24039551	0.00064325	O-1s	0.28384961	0.00026047
(R_{OH} = 1.54774058)		OH	1.22874999	0.80380615		(3.92620226)[b]	
		LP-σ	1.26002928	0.43956044		0.10873247	0.00026047
		(LP $\angle$ = 120°)				(5.18162571)[b]	
		π[c]	1.06572082	±0.1	OH	1.22806945	0.80410810
					LP-σ	1.26131713	0.43956044
					(LP $\angle$ = 120°)		
					π[c]	1.05738035	±0.1

[a] This distance refers to the distance of the FSGO from the heavy atom nucleus. All distances and energies, unless otherwise stated, are given in hartree atomic units; see ref 15. [b] This is the linear coefficient (a_i) in the expression $\varphi = a_1G_1 + a_2G_2$. [c] These π orbitals are formed using the description given in eq 2. [d] These particular fragment parameters were not needed in these calculations but are listed here for completeness.

Molecular Fragments

A description of the three molecular fragments that are needed for these studies is given in Table I, along with the optimized nonlinear parameter values[15] as determined in previous studies.[2,7] The designation "non-split" refers to the use of a single FSGO to describe the inner shell orbital on the heavy nucleus (oxygen or carbon). The other descriptor, "split-1s," corresponds to the use of a normalized linear combination of two FSGO to describe the inner shell orbital on heavy atoms. For this case, the SCF procedure for molecular orbital determination employed the fixed linear combination of two FSGO for heavy atom inner shell orbitals as determined in the fragment studies as a single basis orbital.

The $\cdot OH$ fragment described in Table I corresponds to the one used previously in investigations[7] on several prototype molecules. Such a fragment is depicted pictorially in Figure 1a. However, use of such a fragment for the description of the oxygen environment in a molecule such as CO_2 cannot give acceptable results, since molecular orbitals of the proper symmetry for CO_2 cannot be obtained using the procedure described earlier for construction of large molecules. In addition, electron density contour maps for a variety of molecules containing C=O moieties indicated[7] that, even if the "sp^2"-type fragment description of Figure 1a was employed, the shape of the lone-pair orbitals resulting from the SCF calculations did not resemble "sp^2" hybrids. In particular, these studies revealed that one of the lone-pair orbitals closely resembled a doubly occupied p-type orbital in the σ plane and was localized at the oxygen atom. The other lone-pair orbital also was a doubly occupied orbital that is localized at the oxygen atom but is a σ-type orbital whose centroid is collinear with the C–O bond, and whose density is localized to the side of the oxygen nucleus which is opposite to that of the carbon nucleus. Since this result appeared in general for molecules containing C=O bonds, a molecular fragment corresponding more closely to this description was investigated. A pictorial representation of this "sp"-type fragment is given in Figure 1b. In this fragment, the σ-type lone pair and one of the π-type lone pairs is doubly occupied, and the other π-type orbital is singly occupied. Table II contains the optimized parameters for the "non-split" and "split" representations of this $\cdot OH$ fragment. It should be noted that this fragment description is suitable for construction of CO_2 as well as being consistent with the electron density contours of other molecules containing the C=O moiety.

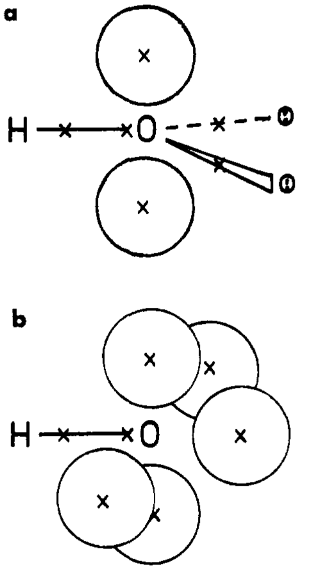

Figure 1. (a) $\cdot OH$ fragment with "sp^2" hybridization of the lone pairs. (b) $\cdot OH$ fragment with "sp" hybridization of the lone pairs.

Molecular Studies

1. Allene and Carbon Dioxide. Since allene and

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(15) All distances and energies are reported in hartree atomic units, unless otherwise specified; see H. Shull and G. G. Hall, *Nature (London)*, 184, 1559 (1959).

Table II. Optimized ·OH (LP-sp) Fragment Data[a]

Description	Orbital type	Orbital radius, ρ	Distance from heavy atom, R	Comments	No. of FSGO
1. "Non-split"	O-atom	0.24028227	0.00057129	R, ρ = freely varied	7
R_{OH} = 1.54774058	OH	1.23671871	0.76467773	R, ρ = freely varied	
E_{tot} = −63.93304110	LP-s	1.28753780	0.21614258	R, ρ = freely varied	
Scale factor = 0.99725247	LP-π (2 electron) occupation	1.19741696	±0.1	ρ = freely varied $R_{LP\pi}$ = chosen as ±0.1 bohr	
	π (1 electron) occupation	1.12242182	±0.1	ρ = freely varied R_π = chosen as ±0.1 bohr	
2. "1s-split"	O-atom $1s_1$	0.28390625 (3.92786307)[b]	0.00022919	R, ρ = freely varied	8
R_{OH} = 1.54774058	$1s_2$	0.10870971 (5.17986942)[b]	0.00022919	R, ρ = freely varied	
E_{tot} = −71.54275608	OH	1.23731923	0.76678006	R, ρ = freely varied	
Scale factor = 0.99748401	LP-s	1.29001792	0.21805665	R, ρ = freely varied	
	LP-π (2 electron) occupation	1.18972158	±0.1	ρ = freely varied $R_{LP\pi}$ = chosen as ±0.1 bohr	
	π (1 electron) occupation	1.11572254	±0.1	ρ = freely varied R_π = chosen as ±0.1 bohr	

[a] All distances and energies are reported in hartree atomic units, unless otherwise stated; see ref 15. [b] Linear coefficients of the FSGO in the "1s-split" description.

Table III. Comparison of SCF Calculations for Allene (D_{2d} symmetry)[a]

	C–H FSGO from			
	CH_4 fragment	CH_3 fragment	Buenker[b]	Peyerimhoff and Buenker[c]
Total energy	−98.993185	−98.888643	−115.6979	−115.8024
Potential energy	−191.286306	−192.630206		
Kinetic energy	92.293121	93.741563		
Nuclear–nuclear energy	59.225571	59.225571		
Electron–nuclear energy	−343.117474	−346.796383		
Electron–electron energy	92.605593	94.940604		
Orbital energies				
$4b_2$	+1.330160	+1.505272		
$5a_1$	+0.905815	+1.039358		
$3e(\pi)$	+0.343980	+0.422024		+0.1676
$2e(\pi)$	−0.256262	−0.176228	−0.4211	−0.3736
$1e(\pi)$	−0.512912	−0.425518 ($3b_2$)	−0.6458	−0.6135
$3b_2$	−0.513629	−0.438655 (1e)	−0.6575	−0.6238
$4a_1$	−0.621677	−0.539855	−0.7389	−0.7112
$2b_2$	−0.915272	−0.807422	−0.9934	−0.9631
$3a_1$	−1.016281	−0.904040	−1.1044	−1.0786
$2a_1$	−9.301631	−9.142949	−11.3465	−11.2406
$1b_2$	−9.436681 ($1a_1$)	−9.244403	−11.3466	−11.2407
$1a_1$	−9.463063 ($1b_2$)	−9.292852	−11.4209	−11.2790

[a] Nuclear coordinates were taken from ref 16. [b] See ref 18. [c] See ref 19.

carbon dioxide represent two of the simplest and best characterized members of the hydrocumulene and oxycumulene series, initial molecular studies were done on these molecules, in order to ascertain the adequacy of the fragment descriptions and the accuracy to be expected.

Table III summarizes electronic structure data from the current studies on allene, along with data from other investigations that have been carried out. As is apparent from the table, use of the CH_4 fragment orbitals for the description of CH bonds, along with the $\cdot CH_3$ fragment orbitals as the other basis orbitals, gives rise to a molecular orbital ordering of valence orbitals in exact agreement with the most extensive calculations available. A similar result has been observed and discussed earlier for the case of benzene and naphthalene isomers.[2b,3] Consequently, the suitability of this choice of fragment description for examination of the electronic structure of hydrocarbon multiple bonds is reaffirmed.

To assess geometric predictive capabilities, two studies were undertaken. The first of these concerns the ability of the procedure to predict angles when C=C multiple bonds are involved, and Figure 2 indicates the dependence of the total energy on the C–C–C angle (ϑ). As observed experimentally,[16] the most stable structure is the linear structure. Also, the barrier to rotation has been examined in the ^1A_g state. The calculated barrier is 75.1 kcal/mol, in excellent agreement with the values reported from other studies (74.61 kcal/mol reported by Andre, *et al.*,[17] 72.7 kcal/

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(16) A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, 17, 136 (1965).

(17) For other recent work on allene see, for example, J. André, M. André, and G. Leroy, *Chem. Phys. Lett.*, 3, 695 (1969); L. J. Schaad, *Tetrahedron*, **26**, 4115 (1970).

Table IV. Comparison of Molecular Orbital Structure for Carbon Dioxide ($D_{\infty h}$ symmetry)

MO symmetry	"Non-split" description $R_{C-O} = 2.1960931$ $\rho_\pi = \rho_{LP\pi}$ $\rho_{LP\pi} = 1.19741696$	 $\rho_{LP\pi} = \rho_\pi$ $\rho_\pi = 1.12242182$	Peyerimhoff, Buenker, and Whitten[a] $R_{C-O} = 2.196$	McLean and Yoshimine[b] $R_{C-O} = 2.1944$	Exptl[c]
$1\pi_g$	−0.226384	−0.178783	−0.5389	−0.54427	−0.5064
$1\pi_u$	−0.483401	−0.446449 ($3\sigma_u$)	−0.7172 ($3\sigma_u$)	−0.71486	−0.6365
$3\sigma_u$	−0.498928	−0.466051 ($1\pi_u$)	−0.7398 ($1\pi_u$)	−0.74341	−0.6634
$4\sigma_g$	−0.558352	−0.509649	−0.7867	−0.80018	−0.7115
$2\sigma_u$	−1.390631	−1.326203	−1.5075	−1.47698	
$3\sigma_g$	−1.434031	−1.375540	−1.5689	−1.52995	
$2\sigma_g$	−9.256397	−9.215446	−11.5322	−11.46013	
$1\sigma_g$	−17.286768	−17.143739	−20.6620	−20.64922	
$1\sigma_u$	−17.348040	−17.205318	−20.6621	−20.64927	
Total energy	−159.9883	−160.032091	−187.4929	−187.72281	

[a] See ref 20. [b] See ref 21. [c] See ref 22.

mol reported by Schaad,[17] and 82.1 kcal/mol reported by Buenker[18,19]). Thus, several electronic and geometric characteristics of allene appear to be well described by the molecular fragment method.

For the case of CO_2, Table IV presents the results for several different fragment possibilities, along with the results of extensive calculations[20,21] and experimental studies[22] for comparison. Both of the current studies listed in Table IV employ the ·OH fragment representation of Table II. However, in order to assure the appearance of molecular orbitals whose symmetries are consistent with those of $CO_2(D_{\infty h})$, the pair of π-type orbitals on the oxygen atoms must be chosen to be identical. Since *a priori* arguments for a choice between the ordinary π-type and the LP-π orbital of the ·OH fragment could not be advanced, both possibilities were investigated. The first column of Table IV corresponds to the choice of the LP-π orbital, and the second column corresponds to the choice of the ordinary π-type orbital for the two π-type basis orbitals on the oxygen atoms. As comparison with both the most accurate calculations and the experimental investigations indicates, the LP-π orbital description provides a valence molecular orbital ordering which is identical to experimental and the most extensive theoretical studies. Thus, within the basis sets employed here, the description of the π orbitals on the terminal oxygens is better described by fragment orbitals that were determined as doubly occupied, instead of singly occupied. These calculations also reinforce the notion[5] that the minimum energy criterion does not necessarily guarantee a balanced basis set, since $E(\rho_\pi = 1.12)$ is lower than $E(\rho_\pi = 1.19)$, but results in an incorrect molecular orbital ordering.

Since geometric questions are also of importance to the study of other oxycumulenes, the energy dependence upon the O–C–O angle in CO_2 was investigated. As Figure 3 indicates, the linear configuration of nuclei is clearly the energy minimum, as expected. Consequently, both geometric and electronic properties of interest to oxycumulene as well as hydrocumulene systems appear to be satisfactorily predicted using the molecular fragment approach.

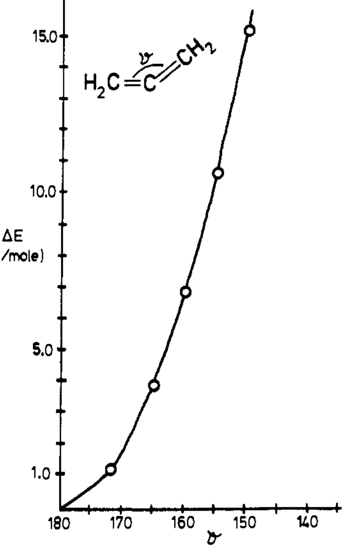

Figure 2. Total energy of allene as a function of the CCC angle (ϑ), relative to the total energy at ϑ = 180°.

2. Acetylene and Ketene. Since interpretation of the charge distributions in cumulenes based upon the use of valence bond structures will frequently invoke structures having triple bonds, it was also deemed important to characterize acetylene itself, to facilitate later comparisons of charge distributions and bond orders. In Table V the resulting MO structure for acetylene is

Table V. Electronic Structure of Acetylene

Current study		Moskowitz[b]	
$R_{CC} = 2.37338430$[a]		$R_{CC} = 2.281$	
$R_{CH} = 2.00314829$		$R_{CH} = 2.002$	
MO structure			
$3\sigma_u$	+0.881638		
$1\pi_g$	+0.337032		
$1\pi_u$	−0.284609	$1\pi_u$	−0.4023
$3\sigma_g$	−0.581278	$3\sigma_g$	−0.6708
$2\sigma_u$	−0.712519	$2\sigma_u$	−0.7588
$2\sigma_g$	−0.972826	$2\sigma_g$	−1.0417
$1\sigma_g$	−9.331768	$1\sigma_n$	−11.2610
$1\sigma_u$	−9.460462	$1\sigma_g$	−11.2646
Total Energy	−65.51814365		−76.760

[a] This CC distance is the equilibrium distance predicted by the molecule fragment method. [b] See ref 23.

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(18) R. J. Buenker, *J. Chem. Phys.*, **48**, 1368 (1968).

(19) S. D. Peyerimhoff and R. J. Buenker, private communication.

(20) S. D. Peyerimhoff, R. J. Buenker, and J. L. Whitten, *J. Chem. Phys.*, **46**, 1707 (1967).

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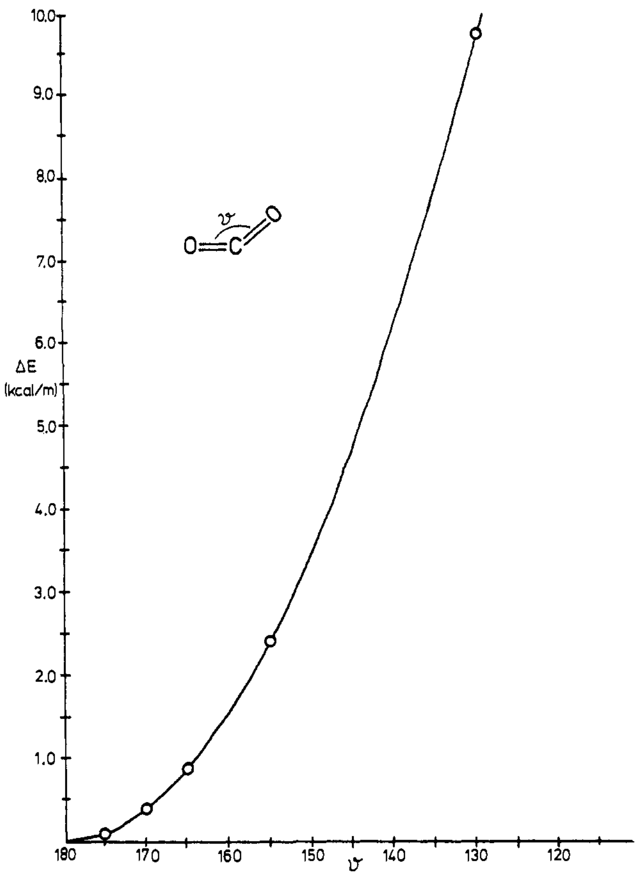

Figure 3. Total energy of CO_2 as a function of the OCO angle (ϑ), relative to the total energy at ϑ = 180°.

given, along with a comparison with the more extensive calculation by Moskowitz.[23] The predicted C–C equilibrium distance is within 4% of the observed value,[24] and the electronic structure of valence molecular orbitals is again found to be in exact agreement with more extensive SCF calculations.

Table VI. Comparison of Calculated Quantities for Ketene[a]

MO symmetry	FSGO description[b] ("non-split")	Letcher, *et al.*[c]
	+0.368678	+0.158119
$2b_1$	−0.176681	−0.343962
$2b_2$	−0.391016	−0.546228
$1b_1$	−0.475899	−0.634406
$1b_2$	−0.513157	−0.653654
$7a_1$	−0.530150	−0.661053
$6a_1$	−0.619757	−0.740288
$5a_1$	−0.956162	−1.053224
$4a_1$	−1.487026	−1.499226
$3a_1$	−9.294303	−11.233078
$2a_1$	−9.428935	−11.395302
$1a_1$	−17.447490	−20.655441
Total energy	−129.504759	−151.507701

[a] Molecular geometry taken from Johnson and Strandberg (see ref 26). [b] The CH FSGO were taken from CH_4, and the ·OH (sp) fragment of Table II was employed. [c] See ref 25.

Finally, since ketene is closely related to the oxycumulenes of this study, and is suggested to have considerable triple-bond character,[25] it was included in the study of prototype molecules. Using the experimental geometry,[26] the results of the current study and the study of Letcher, *et al.*,[25] are given in Table VI. As desired, the molecular orbital ordering is in exact agreement with the more extensive calculation of Letcher, *et al.*

3. Carbon Suboxide. Turning to higher members of the oxycumulene series, it is interesting to consider carbon suboxide (C_3O_2) next. This molecule has been studied rather extensively by a variety of techniques[27–52] in order to determine its electronic and geometric structure. Since many of the difficulties that arise in the interpretation of experimental investigations are associated with the linearity (or lack of it) of C_3O_2, several studies were undertaken to investigate geometric considerations in some detail.

Using the "non-split" fragment description and bond distances given by Tanimoto, *et al.*,[43] the energy dependence on the C–C–C angle (ϑ) was investigated, and the results are summarized in Figure 4. During these particular calculations, the O–C–C angles were maintained at 180°. As the figure shows, the most stable configuration corresponds to a C–C–C angle of 125°, although the energy surface is quite flat between 180° and approximately 115°.

Other investigators have observed a similar behavior. For example, Miller and Fateley[31] suggested on the basis of infrared studies that C_3O_2 may exist in two forms, a linear and a nonlinear form. Also, Clark and Seip[42] recently reported an analysis of spectroscopic and diffraction data and concluded that the potential which described existing data best was one

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(31) F. A. Miller and W. G. Fateley, *Spectrochim. Acta*, **20**, 253 (1964).

(32) W. J. Lafferty, A. G. Maki, and E. K. Plyler, *J. Chem. Phys.*, **40**, 224 (1964).

(33) S. Bell, T. S. Varadarajan, A. D. Walsh, P. A. Warsop, J. Lee, and L. Sutcliffe, *J. Mol. Spectrosc.*, **21**, 42 (1966).

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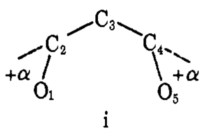
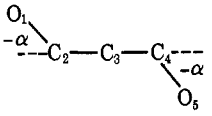
Table VII. Nonlinear C_3O_2 Investigations[a,b]

	ϑ						
α	180 (trans)	180 (cis)	160	150	140	125	120
−8.0	−224.887604	−224.887959	−224.890581	−224.892040	−224.894133	−224.897001	−224.896845
−6.0	−224.890118	−224.890314	−224.892153	−224.893278	−224.895107	−224.897678	*−224.897449*
−4.0	−224.891912	−224.892000	−224.893057	*−224.893860*	*−224.895418*	*−224.897688*	−224.897377
−2.0	−224.892994	−224.893051	*−224.893288*	−224.893768	−224.895060	−224.897020	−224.896627
0.0	*−224.893353*	*−224.893353*	−224.892849	−224.893002	−224.894030	−224.895674	−224.895185
2.0				−224.891562	−224.892319	−224.893631	
4.0				−224.889442	−224.889921	−224.890902	
6.0				−224.886641	−224.886841	−224.887466	
8.0				−224.883158	−224.883070	−224.883327	

[a] Angles are given in degrees. The italicized value in each column is the minimum energy value for that value of ϑ. [b] The angle ϑ is the C–C–C angle. The angle α refers to the deviation of the C–C–O angle from linearity. For $\vartheta \neq 180^c$, positive values of α are defined as shown in structure i. For the special case of $\vartheta = 180°$, we have the trans and cis forms ii and iii.

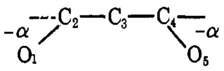


i



trans

ii



cis

iii

in which a nonlinear structure with $\vartheta \simeq 158°$ was most stable, and with a small maximum of approximately 50 cm^{-1} associated with $\vartheta = 180°$. In other studies, Tanimoto, *et al.*,[43] found that a potential having a minimum at $\vartheta = 156°$ and a maximum at $\vartheta = 180°$ of $\simeq$ 100 cm^{-1} was consistent with their electron diffraction data. Also, Almenningen, *et al.*,[39] analyzed the effect of temperature variation on vibrational amplitudes and the effects on the structure of "shrinkage" of various nonbonded distances and concluded that the molecule is probably nonlinear, with $\vartheta \simeq$ 156–148°, and a maximum of 40–255 cm^{-1} at $\vartheta = 180°$. Finally, it might also be noted that the finding by Sabin and Kim[48] of a linear structure in *ab initio* studies is not necessarily inconsistent with the current studies. In particular, the energy dependence at ϑ = 180, 178, and 170° (the angles reported by Sabin and Kim) is quite similar to the corresponding portion of Figure 4, and a search at smaller ϑ may have indicated a behavior similar to that observed in the current calculations. In addition, it is known that the use of off-nuclei FSGO provides a basis set flexibility that is found only when d and higher orbitals are added to atomic orbital basis sets.[7] Since d-orbital effects have been found to be important in the prediction of geometric characteristics in the closely related C_3 molecule,[52a] it is possible that inclusion of d orbitals in atomic orbital bases is needed before comparisons can be made for C_3O_2.

As studies on other prototype molecules have indicated,[2–9] the molecular fragment procedure frequently tends to overemphasize energetic effects associated with conformational changes, *e.g.*, the barrier to rotation in ethane.[2] Thus, the energy of $\simeq$500 cm^{-1} (1.4 kcal/mol) obtained in these studies for 180° (relative to the minimum at $\vartheta = 125°$) may be an exaggeration of this effect. The slight maximum occurring at approximately 155–160° (relative to 180°) is probably too small an effect to be obtained reliably from calculations such as these and may exhibit more of the limit of sensitivity of the method than an actual physical effect.

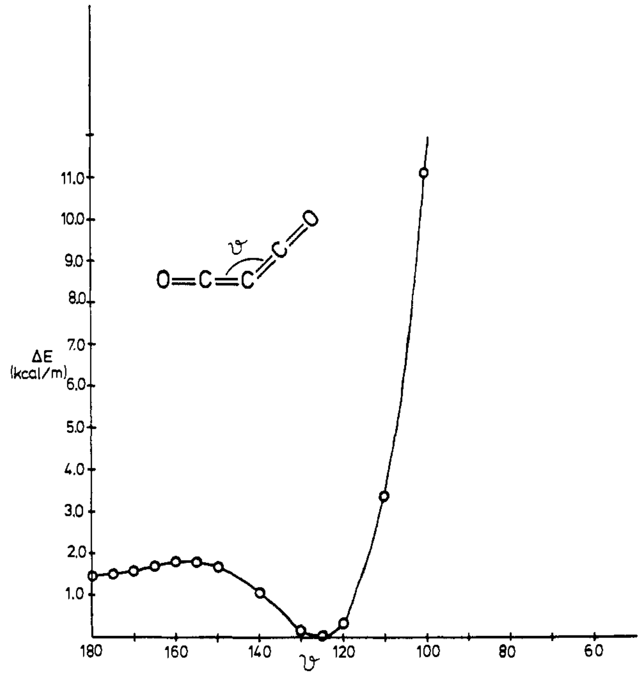


Figure 4. Total energy of C_3O_2 as a function of the CCC angle (ϑ), relative to the total energy at $\vartheta = 125°$.

Finally, the smaller value of ϑ min observed in these calculations ($\vartheta = 125°$), compared to the investigations mentioned previously, was examined in greater detail. The results of these investigations are summarized in Table VII. The first point of interest involves the stability of the trans and cis forms of C_3O_2, relative to the linear structure. Although analysis of the infrared spectra appeared to indicate[31] that both linear and trans (or cis) forms might exist, the current results indicate that, in the gas phase, neither the linear nor the trans (or cis) forms are as stable as the bent structure with $\vartheta \simeq 125°$. Next, we note that the O_1–C_3–O_5 angle is greater than the value of $\vartheta = 125°$, since the optimum value of α is negative. In particular, the O_1–C_3–O_5 angle is approximately 132°, bringing the results of the current studies in closer agreement with the experimental estimates of $\vartheta \simeq 148$–158°.

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Table VIII. Molecular Orbital Structure and Energy Components for Selected Conformers[a] of C_3O_2

Nonlinear C_3O_2 "non-split" description			Linear C_3O_2 (ϑ = 180°, α = 0°)		
MO symmetry	ϑ = 125° α = −4°	ϑ = 125° α = 0°	MO symmetry	"Non-split" description	"Split-1s" description
$7b_1$	+0.374752	+0.384370	$3\pi_u$	+0.632466	+0.532924 ($7\sigma_g$)
			$2\pi_g$	+0.329380	+0.340963
$2a_2(\pi)$	+0.343985	+0.343881	$2\pi_g$	+0.329380	+0.340963
$2b_2(\pi)$	−0.183371	−0.183534	$2\pi_u$	−0.180398	−0.167258
$8a_1$	−0.201982	−0.199937	$2\pi_u$	−0.180398	−0.167258
$6b_1$	−0.430737	−0.430638	$1\pi_g$	−0.438467	−0.425331
$1a_2(\pi)$	−0.440207	−0.440459	$1\pi_g$	−0.438467	−0.425331
$7a_1$	−0.485027	−0.484796	$1\pi_u$	−0.474154	−0.460693
$1b_2(\pi)$	−0.485442	−0.485611	$1\pi_u$	−0.474154	−0.460693
$5b_1$	−0.559625	−0.560553	$5\sigma_u$	−0.560315	−0.552635
$6a_1$	−0.579993	−0.580693	$6\sigma_g$	−0.576123	−0.615810
$4b_1$	−0.754276	−0.754976	$4\sigma_u$	−0.788502	−0.863676
$5a_1$	−1.004114	−1.003452	$5\sigma_g$	−0.954762	−1.072758
$4a_1$	−1.478384	−1.478903	$4\sigma_g$	−1.475027	−1.634708 ($3\sigma_u$)
$3b_1$	−1.479027	−1.479379	$3\sigma_u$	−1.476839	−1.635211 ($4\sigma_g$)
$3a_1$	−9.310869	−9.312510	$3\sigma_g$	−9.316001	−11.114602
$2b_1$	−9.435681	−9.436465	$2\sigma_g$	−9.433507	−11.194112
$2a_1$	−9.451937	−9.453019	$2\sigma_u$	−9.457444	−11.202371
$1a_1$	−17.434592	−17.434518	$1\sigma_g$	−17.432344	−20.790649
$1b_1$	−17.439825	−17.440654	$1\sigma_u$	−17.442523	−20.792579
E_{total}	−224.897688	−224.895674		−224.893354	−251.825054
V_{total}	−437.204941	−437.177859		−436.951469	−497.662329
T	212.307253	212.282195		212.058115	245.837275
V_{N-N}	124.938080	125.154295		121.801066	121.801066
V_{e-e}	207.525698	207.729881		204.495555	206.474768

[a] Distances were held fixed at R_{C-C} = 2.4366599 bohrs, and $R_{C=O}$ = 2.1981718 bohrs, see ref 39.

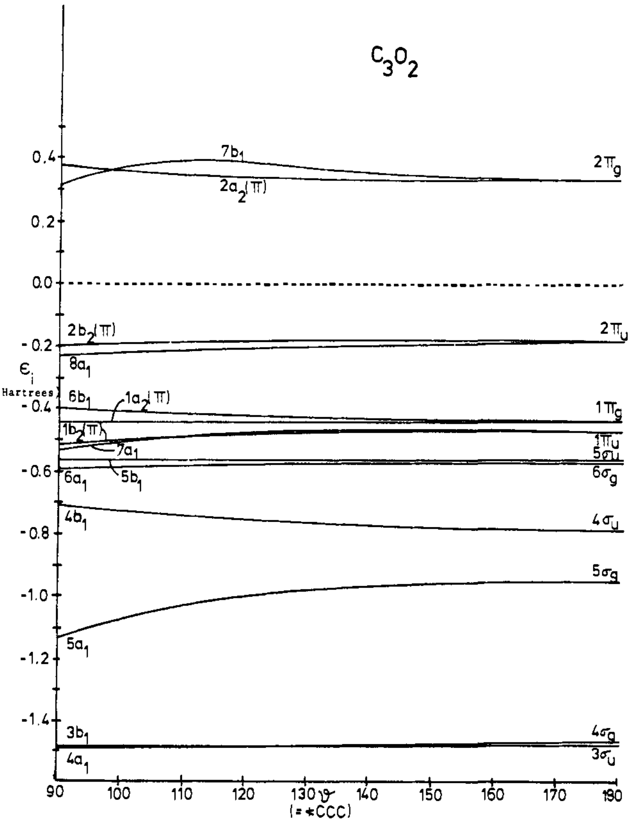

Figure 5. Valence molecular orbital energies of C_3O_2 as a function of the CCC angle (ϑ).

It should be emphasized, however, that the energy curve for bending at the central atom in C_3O_2 is very flat. Thus, the question of the linearity (or lack of it) of C_3O_2 can perhaps be considered to be merely one of semantics. Also, it is not known whether correlation effects that would be obtained using configuration interaction techniques will alter the shape of this curve. Consequently, although it cannot be concluded unequivocally from this study that C_3O_2 must be nonlinear in the gas phase, these results appear consistent with much of the available data, and possibly indicate the need for additional experiments. In the following discussion, it will be shown that, not only the geometric data, but also the electronic structure data for the bent structure are consistent with available experimental data.

The results of electronic structure investigations of various conformers of C_3O_2 are summarized in a Walsh-type diagram (Figure 5) and Table VIII. The first column of the table represents the calculated molecular orbital structure for the most stable structure found in these investigations (ϑ = 125°, α = −4°). The next column represents the most stable structure with α = 0, and the next two columns represent the molecular orbital structure of the linear structure in the "non-split" and "split-1s" description. For the linear case, the molecular orbital ordering is in excellent agreement with other *ab initio* calculations,[46,48] the only disagreement occurring for the case of the nearly degenerate and low-lying $4\sigma_g$ and $3\sigma_u$ orbitals in the "non-split" representation. For the nonlinear configurations, the molecular orbital ordering is also found to be in agreement with other *ab initio* calculations,[48] with the possible exception of the nearly degenerate $7a_1$ and $1b_2(\pi)$ orbitals.

Even though the overall molecular orbital structure (for the linear structure) is the same for the several *ab initio* procedures,[46,48] the predicted equilibrium geometries differ somewhat, as pointed out earlier. A possible explanation for the differences in the geometric predictions of the *ab initio* results was given earlier, and it appears that the recently reported ESCA experimental data[46] may also be consistent with the current studies of electronic structure. In particular, the calculated splittings of the $1\pi_u$ and $1\pi_g$ orbitals for $\vartheta \simeq 125°$ (Table VIII) are small enough that detection of them would be quite difficult in an ESCA experiment. Furthermore, these peaks appear[46] as a shoulder on a much larger peak (attributed to electrons from $6\sigma_g$ and $5\sigma_u$ orbitals), making resolution of any splitting even more difficult. On the other hand, the calculated splitting of the $2\pi_u$ orbital into $2b_2(\pi)$ and $8a_1$ orbitals is larger ($\sim$0.5 eV) than the splitting of the $1\pi_u$ and $1\pi_g$ orbitals, and the $2\pi_u$ peak appears at a place in the ESCA spectrum where resolution of a splitting might be possible. Unfortunately, sufficient resolution is not available (>0.5 eV) to discern both peaks.[46] Consequently, high resolution experiments would be of great help in examining this possibility in greater detail.

It is also of interest to note that the various *ab initio* results,[46,48] including the current study, are not in agreement with the results of extended Hückel theory[50] and CNDO/2,[50] where the following valence electronic structure is observed for the linear configuration:

EHT:

$$(3\sigma_u)^2(4\sigma_g)^2(5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(1\pi_u)^4(1\pi_g)^4(5\sigma_u)^2(2\pi_u)^4$$

CNDO/2:

$$(3\sigma_u)^2(4\sigma_g)^2(5\sigma_g)^2(4\sigma_u)^2(1\pi_u)^4(6\sigma_g)^2(1\pi_g)^4(3\sigma_u)^2(2\pi_u)^4$$

Since the *ab initio* studies have employed a variety of basis sets, and also are consistent with available data from ESCA experiments,[46] it seems likely that the molecular orbital structure as predicted from both extended Hückel theory and CNDO/2 is incorrect, with the π orbitals predicted to be too stable, relative to the σ orbitals.

4. C_5O_2. To investigate whether the next higher member in the "odd" oxycumulene system would exhibit characteristics similar to carbon suboxide, several studies were undertaken on the C_5O_2 molecule using the "non-split" representation. While the existence of this molecule has been reported or inferred on several occasions,[54,55] detailed geometric and electronic structure characterizations have apparently not been carried out. First, the bending motion about the central carbon atom ($O_1{=}C_1{=}C_2{=}C_3{=}C_4{=}C_5{=}O_2$) was investigated, while all other angles were fixed at 180°. The results are displayed in Figure 6a and clearly indicate the preference for a linear $C_2{=}C_3{=}C_4$ moiety. Next, the $C_2{=}C_3{=}C_4$ moiety was fixed in a linear arrangement, and the energy dependence on bending of the C=C=O moiety relative to the $C_2{=}C_3{=}C_4$ moiety in the "cis" and "trans" forms was investigated. The results of these studies are given in Figure 6b, and indicate the preference for a bent structure having $\vartheta \cong 120°$ in both the "cis" and "trans" forms. As noted previously, it is expected that the magnitude of the energy differences in Figure 6 may be overestimated, but the general shapes of the curves are expected to be reliable. The slight dip around $\vartheta = 180°$ for the "cis" form, as in the case of C_3O_2, is believed to be outside the error limits of the calculations, and probably is not significant. Hence, bending at carbons C_2 and C_4 in C_5O_2 seems to have some similarity to the bending at the central atom in carbon suboxide, except that the energies required to make the molecule linear are higher, and the equilibrium angle for C_5O_2 is further from 180° than in C_3O_2. Finally, the "trans" form of C_5O_2 is found to be slightly more stable than the "cis" form (at $\vartheta = 120°$), by an amount of 3.3 kcal/mol.

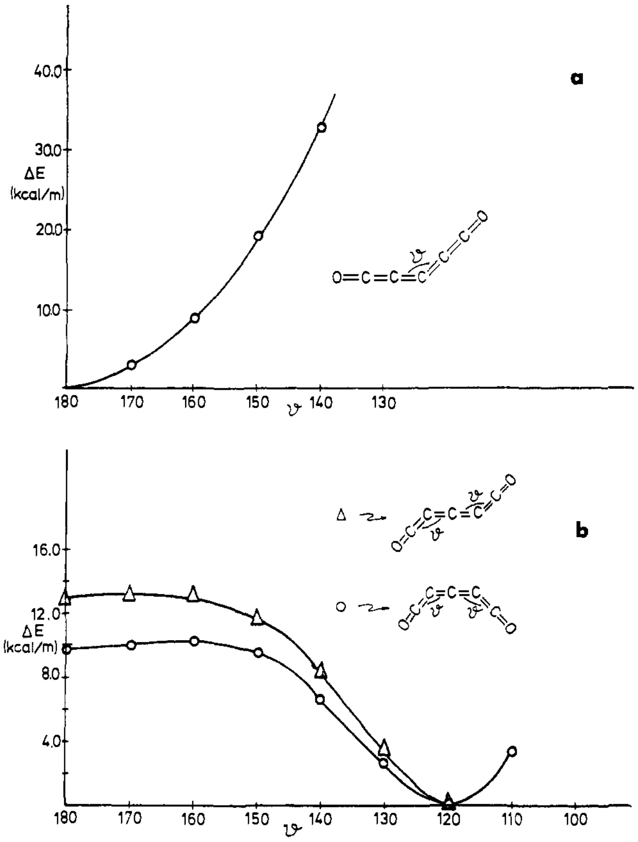

Figure 6. (a) Total energy of C_5O_2 as a function of the $C_2C_3C_4$ angle (ϑ), relative to the total energy at $\vartheta = 180°$. (b) Total energy of "cis" and "trans" C_5O_2 as a function of the $C_1C_2C_3$ angle (ϑ), relative to the total energy at $\vartheta = 120°$.

Discussion

In discussing these calculations, it should be remembered that the basis sets employed here are not large. Consequently, although considerable effort has been expended to assure the appropriateness of the basis *via* studies on prototype molecules, effects resulting from enlargement of the basis remain a possibility. Within this possible limitation, however, the current calculations, which investigate a reasonably large number of cumulenes with basis sets of similar quality, allow interesting comparisons to be made among several of the molecules. For example, the isoelectronic molecules allene, ketene, and carbon dioxide are particularly good candidates for comparative studies, since the correlation energy error might be expected to be approximately constant when comparing these molecules.

In Figure 7 the molecular orbital structures of allene and ketene are correlated as a function of the atomic number of one of the terminal "heavy atoms." One of the interesting aspects of this figure is that the molec-

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(54) A. Klemenc and G. Wagner, *Chem. Ber.*, 70, 1880 (1937); see also O. Diels, *ibid.*, 71, 1197 (1938).

(55) M. Saporoschenko, *J. Chem. Phys.*, 49, 768 (1968).

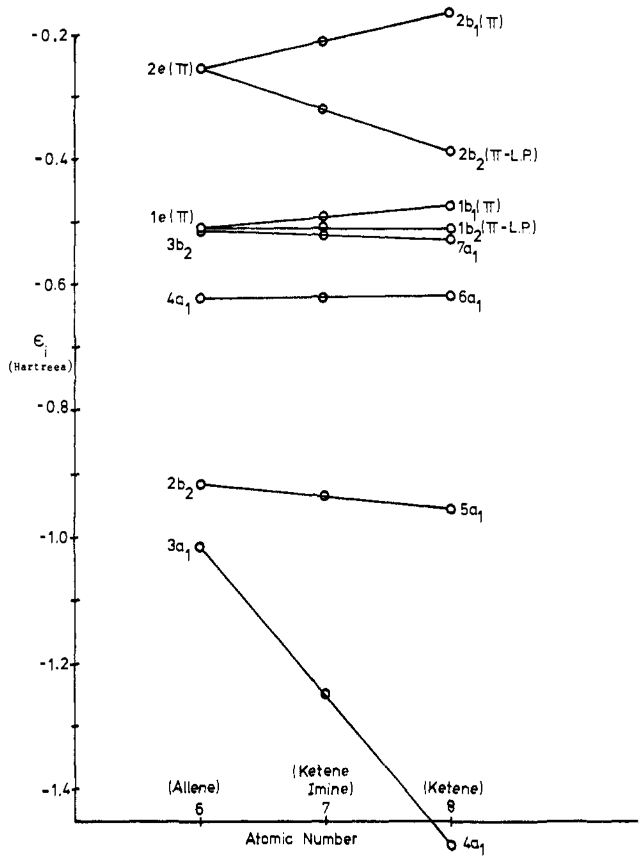

Figure 7. Correlation diagram for valence molecular orbitals of "allene-like" structures as a function of the atomic number of one of the terminal atoms. The points for ketenimine are interpolated from the calculated values for allene and ketene.

ular orbital structure of the ketenimine molecule ($H_2C{=}C{=}NH$), which was not included in the SCF calculations, can be predicted from the figure. While it is certainly possible that some curvature in the lines representing the various correlations in Figure 7 might result if an explicit SCF calculation were carried out on $H_2C{=}C{=}NH$, it seems unlikely that the basic molecular orbital structure of $H_2C{=}C{=}NH$ will be altered.

Also, the magnitude of the various orbital energies in ketenimine can be further quantified. It has been observed that, for a wide range of molecules,[56] the molecular orbital eigenvalues resulting from the molecular fragment approach are related linearly to the accurate Hartree–Fock eigenvalues. Thus, it is possible to obtain a more quantitative estimate of the MO eigenvalues for $H_2C{=}C{=}NH$ by finding the slope and intercept of the linear relations that can be established for allene and ketene. For allene, the slope and intercept are found to be approximately +0.9084 and −0.147, respectively, with a root-mean-square error of ≃0.011. The calculations of Peyerimhoff and Buenker[19] were used for comparison in this case. For ketene, the slope and intercept were found to be approximately +0.8787 and −0.201, respectively, with a root-mean-square error of ≃0.008. The calculations of Letcher, *et al.*,[25] were used for comparison in this case. Since the values are quite similar, it seems likely that average values of +0.8936 and −0.174 for the slope and intercept, respectively, would be appropriate for ketenimine, considering the approximate nature of the discussion at the moment. A summary of the molecular orbital structure of ketenimine that is predicted from this average slope and intercept is given in Table IX. This corresponds to an ionization potential of 9.89 eV for removal of an electron from the $2b_1(\pi)$ molecular orbital.

Table IX. Predicted Valence Molecular Orbital Structure of Ketenimine ($H_2C{=}C{=}NH$)

Molecular orbital[a]	Orbital energy (FSGO)[b]	Orbital energy (extrapolated)[c]
$2b_1$ (π)	−0.212	−0.363
$2b_2$ (π-LP)	−0.323	−0.463
$1b_1$ (π)	−0.494	−0.615
$1b_2$ (π-LP)	−0.512	−0.632
$7a_1$	−0.523	−0.641
$6a_1$	−0.623	−0.731
$5a_1$	−0.936	−1.010
$4a_1$	−1.250	−1.291

[a] The designation "π" refers to MO's containing p orbitals perpendicular to the plane containing the nuclei. The designation "π-LP" refers to MO's containing p orbitals (and s orbitals) in the plane containing the nuclei. [b] Obtained from Figure 7. [c] Obtained from the relation ϵ_i (extrapolated) = $+0.8936\epsilon_i$(FSGO) − 0.174. See the text for further discussion.

The results of these studies can also be used to show several points of interest regarding the similarities and differences in the charge distribution and chemical bonding in the various cumulenes. In Figure 8 is given the electron population of the various FSGO (symmetrically orthogonalized), where the population in the bonding region between "heavy" atoms is taken as the sum of the populations of the two orbitals in that region.[56] Also, the bond orders[56] for the various bonds in the molecule are given in Table X. The first group of molecules in the table (ethylene, allene, and ketene) form prototypes for "typical" C=C and C=O double bonds, while acetylene serves as a prototype for a triple bond, and CO_2 falls somewhere in between, having some double and some triple bond character.

Comparing the other cumulenes to these prototypes, we note first that the changes in bonding that occur are essentially all contained in changes in π-bond orders and populations, while the σ-bond orders and populations remain effectively constant throughout the series. Next, we note from the bond orders in Table X that the cumulated =C=O bonds in ketene, C_3O_2, and C_5O_2 are all nearly identical, and have considerable triple bond character. This is consistent with the results of the CNDO/2 study,[50] and the relationship of the triple bond character to bending motions at the carbonyl carbon will be explored shortly. Also, we note that the bond orders in C_3O_2 remain essentially constant when the molecule is bent, although there is a considerable negative charge at the central carbon atom (which favors a bent structure[57]), as observed by others,[46,48,50] and which increases upon bending. Finally, we note that the cumulated =C=C= bonds in C_3O_2 and C_5O_2 are not all alike but fall into roughly two

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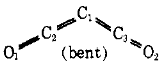
(56) L. L. Shipman and R. E. Christoffersen, *J. Amer. Chem. Soc.*, **95**, 1408 (1973).

(57) K. S. Pitzer and S. J. Strickler, *J. Chem. Phys.*, **41**, 730 (1964).

Table X. Bond Orders in Various Cumulenes

Molecule	C=C bond orders σ	C=C bond orders π	C=C bond orders Total	C=O bond orders σ	C=O bond orders π	C=O bond orders Total
$H_2C{=}CH_2$ M	0.96	1.00	1.96			
$H_2C{=}C{=}CH_2$	0.97	0.95	1.92			
$H_2C{=}O$				0.95	1.00	1.95
$HC{\equiv}CH$	0.97	2.00	2.97			
CO_2				0.93	1.42	2.35
$H_2C{=}C{=}O$	0.95	0.73	1.68	0.94	1.62	2.56
$O_1{=}C_2{=}C_1{=}C_3{=}O_2$	0.96	1.10	2.06	0.95	1.62	2.57
	0.95	1.06	2.01	0.94	1.62	2.56
$O_1{=}C_1{=}C_2{=}C_3{=}C_4{=}C_5{=}O_2$	0.98 $(C_2{=}C_3)$	1.30	2.28	0.95 $(O_1{=}C_1)$	1.64	2.59
	0.96 $(C_1{=}C_2)$	1.04	2.00			

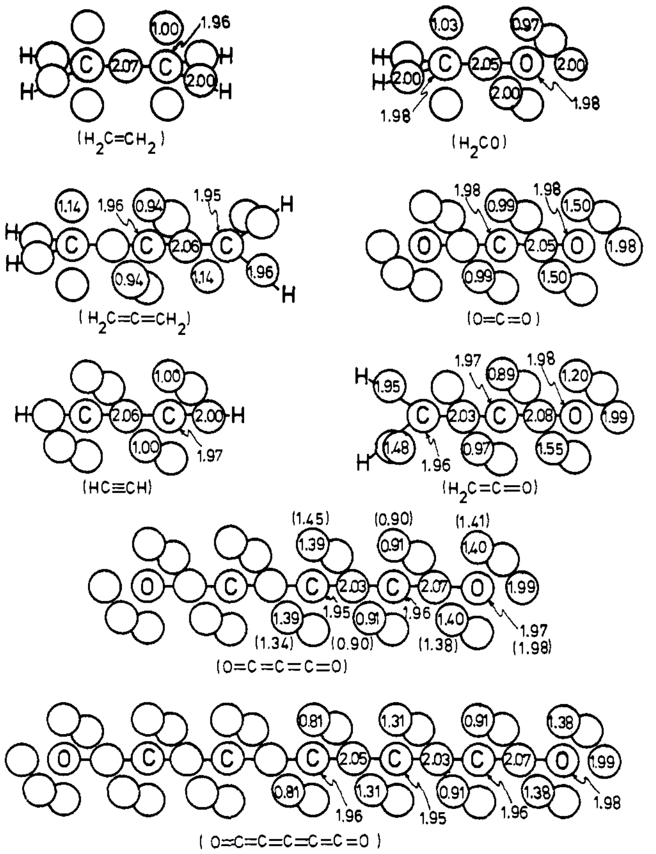


Figure 8. Orbital populations for symmetrically orthogonalized orbitals for cumulenes and related molecules. The numbers in parentheses for C_3O_2 represent the orbital populations for the bent structure (ϑ = 125°) for those orbitals whose occupation changes from that in the linear structure.

types. In particular, the $C_2{=}C_1$ in C_3O_2 is quite similar to the $C_1{=}C_2$ (and $C_4{=}C_5$) bonds in C_5O_2. These bonds possess considerably less triple bond character than the $C_2{=}C_3$ bond in C_5O_2. Thus, the bonds in cumulenes should not be considered to be all equivalent "double" bonds but a reasonably regular *mixture* of bonding types, and nonlinear structures under these circumstances should not be considered particularly unusual.

These bond orders and calculated energies required for bending at the various carbon atoms within cumulenes also suggest several generalizations. In particular, it appears from these studies that at least two kinds of bending motions are observed, and these are shown in the graphs of Figures 9a and 9b, where the bending motions for the molecules of this study are summarized. The first of these, which can be referred to as a "high energy" bend, is typified by allene, CO_2, and bending about the central carbon atom in C_5O_2. The other bending motion, which can be referred to as a "low energy" bend, is observed in bending around the central carbon atom in C_3O_2, and about the carbons labeled C2 and C4 in C_5O_2. This latter type motion also is observed in related molecules, such as the C_3 molecule.[58]

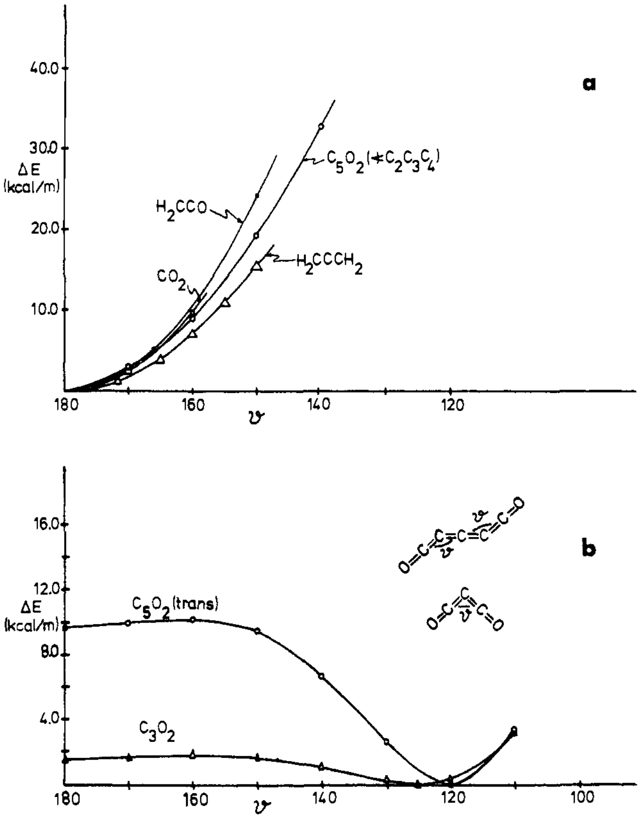


Figure 9. (a) Angle bending comparisons for allene, ketene, CO_2, and C_5O_2 ($\angle C_2C_3C_4$). (b) Angle bending comparisons for C_3O_2 and "trans" C_5O_2 ($\angle C_1C_2C_3$).

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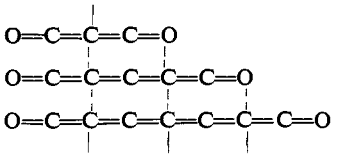
(58) L. Gausset, G. Herzberg, A. Lagerqvist, and B. Rosen, *Discuss Faraday Soc.*, No. 35, 113 (1963).

These two qualitatively different kinds of bending potentials seem to indicate the possibility of two kinds of moieties that might be identifiable in oxycumulenes in general. The first is a ketene-type moiety (=C=C=O), which favors a linear structure. The second is an allene-type structure (=C=C=C=), which also favors a linear configuration. At the juncture of these moieties, however, low bending force constants may be found. This would lead to a general view of oxycumulenes as



etc.

where facile bending would be expected at the carbon atoms that join the ketene and allene moieties. However, considerable further investigation may be needed to test the generality of this notion.

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Electrostatic Force Theory for a Molecule and Interacting Molecules. III. Overlap Effect on the Atomic Dipole and Exchange Forces, Orbital Following and Preceding, and the Shapes of X_mABY_n Molecules

Hiroshi Nakatsuji

Contribution from the Department of Hydrocarbon Chemistry,
Faculty of Engineering, Kyoto University, Kyoto, Japan.
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Abstract: This paper treats an extension of the electrostatic force (ESF) theory proposed previously.[1] First, the effect of orbital overlap (named *overlap effect*) on the atomic dipole (AD) and exchange (EC) forces is examined. The effect is proved to have wide applicabilities for both molecular structure and chemical reaction. Especially the π-overlap effect may be considered as the "conjugation effect" in comparison with the inductive substituent effects on the AD and EC forces summarized previously. Moreover, the overlap effect on the EC force manifests itself in many important aspects of chemical reaction and molecular interaction (*e.g.*, conservation of molecular orbital symmetry, non-least-motion reaction path, exchange repulsion, etc.). Another manifestation of the overlap effect is the orbital following and preceding in the problem of internal rotation barrier. Generally, the *orbital following*, which means the incomplete following of (local) electron distribution to a movement of nuclei, causes forces that *restrain* the movement of nuclei. On the other hand, the *orbital preceding*, which means the preceding of (local) electron distribution to a movement of nuclei, causes forces that *promote* the movement of nuclei. These orbital following and preceding are proved to be a dominant origin of the rotational barrier in many important cases except for the internal rotation about the single bond. General features in the internal rotation about the single bond are also studied, and three factors are pointed out as important. Based on the ESF theory reinforced by the above considerations, the shapes of X_mABY_n molecules are discussed. The results are generally satisfactory.

In the previous two papers of this series,[1] the electrostatic force (ESF) theory in which chemical phenomena are studied through force concept (not through energetics) has been developed and applied mainly to the shapes of the ground and excited states of a wide variety of AX_n molecules. The basis of the theory is the Hellmann–Feynman theorem[2,3] expressed in atomic units by

$$\mathbf{F}_A = Z_A\left\{\int \rho(\mathbf{r}_1)\mathbf{r}_{A1}/r_{A1}{}^3\,d\mathbf{r}_1 - \sum_{B(\neq A)} Z_B\mathbf{R}_{AB}/R_{AB}{}^3\right\} \quad (1)$$

with the same notations as in paper I. Taking advantage of the physical simplicity and visuality of eq 1, we derived three pictorial concepts called atomic dipole (AD) force, exchange (EC) force, and gross charge (GC) or extended gross charge (EGC) force. The balancing of these forces determines molecular shape. Some regularities in the influences on these forces induced by the change of the concerned atom A and substituent X were summarized. Especially, the shapes of usual molecules were shown to be in close relation with the electron density in the p_π AO of the central atom A in planar or linear structures, which is designated as $D(p_{\pi A})$ (see Figure 7 of paper I). These theoretical concepts were shown to be very useful in predicting the shapes of molecules in both the ground and

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[1] H. Nakatsuji, *J. Amer. Chem. Soc.*, **95**, 345, 354 (1973), which are referred to in the text as papers I and II, respectively.

[2] H. Hellmann, "Einführung in die Quantenchemie," Deuticke, Vienna, 1937; R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939).

[3] A. C. Hurley, "Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., p 161; *Proc. Roy. Soc., Ser. A*, **226**, 170, 179 (1954).