molecules. The C=C (1.347 (4) Å) and C—C (1.502 (3) Å) bond lengths in 2,5-dihydrofuran agree with those in propene (C=C = 1.342 (2) Å and C—C = 1.506 (3) Å)[42] and *cis*-2-butene (C=C = 1.348 (9) Å and C—C = 1.509 (6) Å)[43] within their respective uncertainties. The C=C bond length also agrees with that in cyclopentene (1.342 (10) Å).[7] In contrast with these bond lengths, the C—O bond length (1.440 (2) Å) in 2,5-dihydrofuran is considerably longer than those in dimethyl ether (1.418 (3) Å)[44] and ethyl methyl ether (1.418 (2) Å),[45] and it is even longer than that found in tetrahydrofuran (1.428 (5) Å).[46] Similar lengthening has been observed in the C—Si bond length in silacyclopent-3-ene (1.901 (3) Å)[13] relative to dimethylsilane (r_s = 1.867 (2) Å)[47] and silacyclopentane (1.892 (2) Å).[48] The observed variation of the C—O bond length is rather difficult to explain, but it may be due to bond stretching introduced by trying to accommodate two sp^2 carbon valence angles in a small five-membered ring. This at least would explain the apparent shortening of the C—O bond length in tetrahydrofuran relative to 2,5-dihydrofuran. The unstrained sp^3 valence angles of 109.5° are more easily accommodated without bond stretching than the 120° sp^2 valence angles. This ring strain is further compounded by the larger bending force constant in the unsaturated molecule.

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Registry No. 2,5-Dihydrofuran, 1708-29-8.

Supplementary Material Available: Tables of experimental intensity data and correlation and error matrices (4 pages). Ordering information is given on any current masthead page.

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Structure of Butatrienone ($CH_2{=}C{=}C{=}C{=}O$)

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Abstract: The structure of butatrienone ($CH_2{=}C{=}C{=}C{=}O$) has been determined with the aid of ab initio molecular orbital calculations. An orthogonal-bent structure is predicted. Taken together with previous results for propadienone and new results for pentatetraenone and hexapentaenone, the theoretical result for butatrienone suggests that bending of the heavy-atom chain is a general feature of larger cumulenones $CH_2{=}(C)_n{=}O$. The preferred bending direction alternates as a function of *n* between in-plane and orthogonal.

The structures of cumulenones ($CH_2{=}(C)_n{=}O$, *n* = 0, 1, 2, 3, ...; Figure 1) have aroused considerable theoretical[1-3] and experimental[4-6] interest. Formaldehyde (*n* = 0) and ketene (*n* = 1), of course, have well-established and straightforward structures; however, the structure of propadienone (*n* = 2) is quite unusual. While naively one might expect cumulenones to have a linear chain of heavy (i.e., non-hydrogen) atoms, resulting in molecules with C_{2v} symmetry, experiment[5] and theory[3] now agree that this is *not* the case for propadienone. If fact, this molecule is planar bent with C_s symmetry and a CCC bond angle in the vicinity of 145°.[3]

The structures of higher members of the series are therefore of interest. For instance, the question arises as to whether all or only some of the higher members have nonlinear chains. In this connection, it is well-known that cumulene molecules exhibit alternating properties, according to whether *n* is odd or even. A striking related example is the discovery in interstellar space of HC_nN molecules with *n* = 1, 3, 5, 7, 9 but not with *n* even.[7]

Only one experimental structural result has so far been reported for higher cumulenones.[6] Although the data were limited, they appeared to be consistent with the molecule of butatrienone (*n* = 3) having C_{2v} symmetry and not exhibiting the peculiarities of propadienone. Minimal basis set PRDDO calculations[8] also revealed no evidence for deviations from C_{2v} symmetry. In this paper, we describe the results of a detailed study of butatrienone at significantly higher levels of theory. These indicate an *orthogonal-bent equilibrium structure for butatrienone.*

Method and Results

All calculations were carried out by using a modified version[9a] of the GAUSSIAN 80 system of programs.[9b] In the case of propadienone, we have found previously[3] that the Hartree–Fock model predicts an incorrect structure, namely one with C_{2v} symmetry.[1,2] It is necessary to include correlation energy to obtain the correct result,[3] a situation that is rather unusual. Clearly care must be taken in the calculation on butatrienone to take into account such effects.

In our previous work on propadienone[3] we used the following scheme. Optimized Hartree–Fock (HF) geometries we obtained by using the split-valence 4-31G basis set[10] for a series of structures in which the CCC bond angle was fixed at different values. These structures were then empirically corrected to compensate for systematic deficiencies. Single-point calculations were performed

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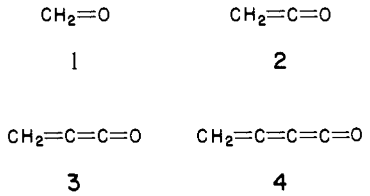

Figure 1. Schematic representation of the cumulenones [$CH_2{=}(C)_n{=}O$; n = 0, 1, 2, 3, and 4]: formaldehyde (**1**), ketene (**2**), propadienone (**3**), and butatrienone (**4**).

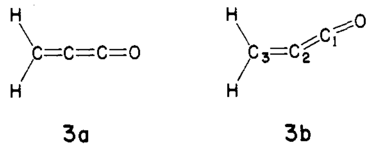

Figure 2. Symmetric (**3a**) and planar-bent (**3b**) structures of propadienone.

Table I. Total Energies (hartrees) and Relative Energies (cm^{-1}) for Symmetric (C_{2v}) and Planar-Bent (C_s, $\angle C_1C_2C_3$ = 170.0°) Structures of Propadienone[a]

	C_{2v} (3a)		C_s (3b)	
	total	relative	total	relative
HF/4-31G	−189.25411	0	−189.25376	77
HF/4-31G[b]	−189.25542	0	−189.25515	59
HF/6-31G	−189.44877	0	−189.44846	68
HF/6-31G[b]	−189.44955	0	−189.44930	55
MP2/6-31G	−189.83823	0	−189.83875	−114
MP2/6-31G[b]	−189.83587	0	−189.83646	−129
MP3/6-31G	−189.83420	0	−189.83451	−68
HF/6-31G*	−189.53361	0	−189.53358	7
MP2/6-31G*	−190.08389	0	−190.08418	−64
MP3/6-31G*	−190.09131	0	−190.09151	−44

[a] Calculated for the empirically corrected structures of ref 3 unless otherwise noted. [b] Calculated for uncorrected 4-31G optimized structures.

on the corrected structures with use of the larger 6-31G* basis set,[11,12] which includes polarization functions on heavy atoms, and with correlation energy incorporated by use of a Møller–Plesset perturbation expansion truncated at third order (MP3).[13,14] The resulting bending potential function allowed a prediction of the optimum CCC angle.

For butatrienone, evaluation of the bending potential function at the MP3/6-31G* level would be prohibitively expensive. However we had noticed, in the case of propadienone, that bending of the heavy-atom chain was predicted even with split-valence basis sets (e.g., 6-31G[10]), provided that electron correlation was taken into account. In other words, although MP3/6-31G* calculations are necessary to get quantitative agreement with experiment, MP2/6-31G and MP3/6-31G calculations give qualitatively correct predictions. We therefore performed calculations at these levels in the present study.

We initially carried out MP2/6-31G and MP3/6-31G calculations for the symmetric C_{2v} (**3a**, Figure 2) and planar-bent ($\angle C_1C_2C_3$ = 170°) C_s (**3b**, Figure 2) structures of propadienone for which we had previously obtained more accurate results.[3] The comparison is presented in Table I and allows some assessment of the reliability of MP2/6-31G and MP3/6-31G results for butatrienone.

In the case of butatrienone, we initially optimized five structures at the HF/4-31G level by using a gradient algorithm.[15] These structures are shown in Figure 3. They are the symmetric C_{2v} structure (**4a**), two planar-bent structures with either $\angle C_1C_2C_3$ (**4b**) or $\angle C_2C_3C_4$ (**4c**) fixed at 170°, and two orthogonal-bent structures again with either $\angle C_1C_2C_3$ (**4d**) or $\angle C_2C_3C_4$ (**4e**) fixed at 170°. Single-point calculations were performed on these optimized structures at the MP2/6-31G level. The results are presented in Table II. Distortion of **4a** to the orthogonal-bent structure **4d** produced a lowering of the energy. Therefore, additional structures of this type were examined with $\angle C_1C_2C_3$ fixed at 165°, 160°, and 150°. These results are presented in Tabel III. Calculated vibrational frequencies, rotational constants, moments of inertia, and dipole moments for butatrienone are displayed in Tables IV–VI, respectively. Our best predicted structure for butatrienone is shown in Figure 4.

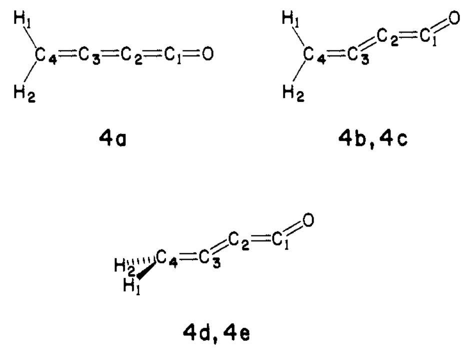

Figure 3. Symmetric (**4a**), planar-bent (**4b**, **4c**), and orthogonal-bent (**4d**, **4e**) structures of butatrienone.

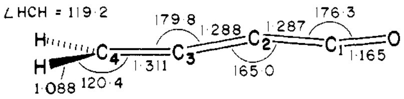

Figure 4. Predicted r_0 structure of butatrienone.

Discussion

The results of Table I show that the lowering of energy accompanying in-plane distortion of C_{2v} propadienone is reproduced at the MP2/6-31G and MP3/6-31G levels. This conclusion is not affected by the use of uncorrected 4-31G optimized geometries in place of empirically corrected structures. Additional calculations[16] show that at the MP2/6-31G level the equilibrium structure of propadienone has $\angle C_1C_2C_3$ = 149° and an inversion barrier of 490 cm^{-1} while at the MP3/6-31G level the values are 160° and 167 cm^{-1}, respectively, compared with our best predictions[3] of 145° and 371 cm^{-1}, respectively, and experimental values[5,17] and 150° and 377 cm^{-1}, respectively. These comparisons provide a basis for expecting at least qualitative reliability for our MP2/6-31G and MP3/6-31G predictions for butatrienone.

In the case of butatrienone, an energy lowering is observed (Table II) for an *orthogonal-bent* (**4d**) rather than a planar-bent (**4b**) distortion. The structure of minimum energy (cf. Table III) lies in the vicinity of $\angle C_1C_2C_3$ = 161°, with a barrier to inversion of about 433 cm^{-1}, at the MP3/6-31G level; corresponding values at MP2/6-31G are 160° and 504 cm^{-1}. As for propadienone (Table I), addition of polarization functions is found to provide relative stabilization to the bent geometries of butatrienone,[18] thus reinforcing our prediction of a preferred orthogonal-bent structure.

The planar and orthogonal distortions in propadienone and butatrienone, respectively, are compatible with the structural alternation well-known for ethylene and allene. They are also consistent with the calculated vibrational frequencies. The HF/3-21G frequencies for the C_{2v} structure[19] (**3a**) of butatrienone

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(18) The energy difference between structures with $\angle C_1C_2C_3$ = 165° and 180° is 19 cm^{-1} at the HF/6-31G* level, compared with 80 cm^{-1} at HF/6-31G (Table III).

(19) Re-optimized at the HF/3-21G level.

Table II. Optimized Geometric Parameters,[a,b] Total Energies (hartrees), and Relative Energies (cm^{-1}) for Butatrienone Structures

	4a	4b	4c	4d	4e
			Geometric Parameters		
$C_1{-}O$	1.168	1.168	1.168	1.168	1.169
$C_1{-}C_2$	1.263	1.263	1.263	1.265	1.262
$C_2{-}C_3$	1.266	1.267	1.267	1.267	1.267
$C_3{-}C_4$	1.297	1.297	1.298	1.297	1.298
$C_4{-}H_1$	1.071	1.071	1.072	1.071	1.071
$C_4{-}H_2$	1.071	1.071	1.070	1.071	1.071
$\angle OC_1C_2$	180.0	180.0	177.0	177.2	179.2
$\angle C_1C_2C_3$	180.0	170.0[c]	179.4	170.0[c]	179.0
$\angle C_2C_3C_4$	180.0	178.9	170.0[d]	180.0	170.0[d]
$\angle C_3C_4H_1$	121.0	121.0	119.6	121.0	120.9
$\angle C_3C_4H_2$	121.0	120.9	122.4	121.0	120.9
$\angle H_1C_4H_2$	118.0	118.1	118.0	118.0	118.0
			Total Energies		
HF/4-31G	−227.04863	−227.04778	−227.04650	−227.04861	−227.04668
HF/6-31G	−227.28263	−227.28177	−227.28055	−227.28260	−227.28076
MP2/6-31G	−227.75581	−227.75572	−227.75472	−227.75729	−227.75536
			Relative Energies		
HF/4-31G	0	187	468	4	428
HF/6-31G	0	188	457	6	410
MP2/6-31G	0	20	239	−324	99

[a] HF/4-31G. [b] Throughout this paper, bond lengths are in angstroms and bond angles are in degrees. [c] $\angle C_1C_2C_3$ fixed at 170°. [d] $\angle C_2C_3C_4$ fixed at 170°.

Table III. Optimized Geometric Parameters, Total Energies (hartrees), and Relative Energies (cm^{-1}) for Orthogonal-Bent (4d) Structures of Butatrienone

			Geometric Parameters[a]		
$\angle C_1C_2C_3$[b]	180.0	170.0	165.0	160.0	150.0
$C_1{-}O$	1.168	1.168	1.168	1.167	1.164
$C_1{-}C_2$	1.263	1.265	1.267	1.269	1.277
$C_2{-}C_3$	1.266	1.267	1.268	1.270	1.275
$C_3{-}C_4$	1.297	1.297	1.296	1.296	1.295
$C_4{-}H_1$	1.071	1.071	1.071	1.071	1.071
$C_4{-}H_2$	1.071	1.071	1.071	1.071	1.071
$\angle OC_1C_2$	180.0	177.2	176.2	175.4	173.8
$\angle C_2C_3C_4$	180.0	180.0	180.1	179.8	180.0
$\angle C_3C_4H_1$	121.0	121.0	121.0	121.0	121.0
$\angle C_3C_4H_2$	121.0	121.0	121.0	121.0	121.0
$\angle H_1C_4H_2$	118.0	118.0	118.0	118.0	117.9
			Total Energies		
HF/4-31G	−227.04863	−227.04861	−227.04822	−227.04751	−227.04489
HF/6-31G	−227.28263	−227.28260	−227.28226	−227.28155	−227.27895
MP2/6-31G	−227.75581	−227.75729	−227.75795	−227.75811	−227.75732
MP3/6-31G	−227.74678	−227.74812	−227.74869	−227.74874	−227.74763
			Relative Energies		
HF/4-31G	0	4	90	246	821
HF/6-31G	0	6	80	238	809
MP2/6-31G	0	−324	−470	−504	−332
MP3/6-31G	0	−293	−419	−430	−185

[a] Units as in Table II. [b] Fixed bending angle.

Table IV. Calculated Vibrational Frequencies (HF/3-21G, cm^{-1}) for C_{2v} Butatrienone (4a)

a_1	b_1	b_2
3322	982	3404
2490	627	1145
2214	554	803
1652	86	480
1509		160
816		

are listed in Table IV. They indicate that the out-of-plane bending motion (b_1 symmetry) is easier than the in-plane motion (b_2 symmetry), which is the reverse of the result for propadienone.[2] It is interesting that the alternation between in-plane and out-of-plane low-frequency bending motions continues in ketene for which the experimentally derived out-of-plane hydrogen bending force constant is very low.[20]

Since the microwave spectrum of butatrienone has been interpreted[6] as consistent with a C_{2v} structure and has been contrasted with the planar-bent structure of propadienone, we must ask whether our conclusion is compatible with this. First we note that part of the evidence for bending in propadienone was the observation of cis and trans isomers of the monodeuterated species. Because the bending in butatrienone is in the orthogonal direction, the hydrogen atoms remain equivalent, and these considerations do not apply.

Second, we can evaluate rotational constants as a function of bending. For this purpose, an empirical correction is applied to the geometry, as previously described,[3] to take account of systematic deficiencies of HF/4-31G geometry predictions. The corrections applied are +0.017 (C–H lengths), +0.020 (C_1–C_2 and C_2–C_3), +0.015 (C_3–C_4), −0.003 (C_1–O), and −0.6 (CCH angles). The computed rotational constants are presented in Table V together with relevant experimental data. It can be seen that near 165° we get agreement with the experimental B_0 and C_0 values to about 0.005 GHz, an accuracy similar to that achieved for propadienone.[3] For the C_{2v} structure, on the other hand, the

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Table V. Rotational Constants (GHz) for Isotopically Substituted Orthogonal-Bent Structures (4d) of Butatrienone as a Function of the $C_1C_2C_3$ Bond Angle

	H_2CCCCO			HDCCCCO			D_2CCCCO		
$\angle C_1C_2C_3$, deg	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
180	284.7	2.138	2.122	193.5	2.051	2.030	142.5	1.974	1.947
170	235.1	2.145	2.132	167.7	2.057	2.038	127.1	1.980	1.955
165	195.9	2.157	2.148	146.8	2.069	2.054	114.8	1.991	1.970
160	156.4	2.173	2.170	122.8	2.085	2.075	99.2	2.006	1.990
150	99.8	2.233	2.218	84.1	2.136	2.127	71.8	2.048	2.048
exptl[a]		2.161	2.147		2.074	2.054		1.996	1.971

[a] Reference 6.

Table VI. Comparison of Calculated and Experimental Moments of Inertia (amu Å^2) and Dipole Moments (D)

quantity	species	calcd[a]	exptl[b]
I_a	H_2CCCCO	2.580	1.605
	HDCCCCO	3.444	2.980
	D_2CCCCO	4.403	3.736
μ_a	H_2CCCCO	2.652[c]	1.967
	HDCCCCO	2.652[c]	1.953
	D_2CCCCO	2.653[c]	1.966
$\lvert\mu\rvert$	all	2.668[c]	

[a] Calculated for the structure shown in Figure 4. [b] Reference 6. [c] HF/6-31G$^+$.

calculated constants are systematically too low by about 0.025 GHz.

Although the B_0 and C_0 constants are consistent with an orthogonal-bent structure, there does appear to be a problem with A_0. Brown et al.[6] do not give A_0, but they do give the related moments of inertia I_a. These are presented in Table VI. The calculated values are considerably different from the experimentally obtained numbers. However, this may simply reflect the difficulty in extracting a reliable *A* rotational constant from the available experimental data. Thus, all of the observed transitions are *a* type and belong to the *R* branch; as a consequence, only the *B* and *C* rotational constants can be determined with confidence.

We have attempted to simulate the microwave spectrum of butatrienone ourselves, using a somewhat different Hamiltonian from that of Brown et al. Our Hamiltonian is basically that previously used for ketene,[21] but incorporating certain octic distortion constants. The computer program was tested by reproducing published analyses of the spectra of ketene[21,22] and propadienone.[5] For butatrienone, we find that *A* is strongly correlated with the quartic distortion constant D_2 (= R_5)[23]. By fixing D_2 at different values, *A* can be varied over a wide range, including the values calculated for our 165° orthogonal–bent structure, while maintaining a good fit to the data.

A further point is that the reported I_a values[6] for H_2CCCCO and D_2CCCCO are themselves not consistent with a C_{2v} structure for which they should be in the ratio $m_D/m_H = 2.0141/1.0078$, or 2.00:1. The ratio of the reported values is 2.33:1 which may be compared with 2.00:1 for ketene.[22] Although this deviation may be due in part to large vibrational effects, it is clear that more experimental data are required to sort out satisfactorily the various hypotheses.

We have calculated the dipole moment at the HF/6-31G$^+$ level for butatrienone with $\angle C_1C_2C_3 = 165°$. Previous results for lower cumulenones[3] indicate that at this level the calculated value is about 25% too large. Since only the component μ_a has been determined experimentally, a comparison for this quantity is given in Table VI. While the calculated values are somewhat higher than might have been expected, experiment and theory agree that there is little variation between isotopic species. Also we predict that any transverse components of dipole moment are much smaller than those found for propadienone.[3,6] The dipole moment decreases slowly as a function of the orthogonal bending angle, i.e., there is improved agreement with experiment accompanying bending.

On the basis that the rotational constants are best fitted with $\angle C_1C_2C_3 = 165°$, we choose this geometry as our best prediction for the butatrienone molecule. Our predicted structure, which includes the empirical corrections, is shown in Figure 4.

Finally, we note preliminary results for the next members of the series, namely pentatetraenone ($CH_2{=}C{=}C{=}C{=}C{=}O$) and hexapentaenone ($CH_2{=}C{=}C{=}C{=}C{=}C{=}O$). Both of these molecules are found to be bent, *even at the HF/4-31G level.* The preferred bending directions are respectively planar and orthogonal. Thus, it seems that bending of the heavy-atom chain is characteristic of cumulenones. It also seems likely that the preferred direction of the distortion alternates as a function of chain length between in-plane and out-of-plane.

Conclusion

The molecule of butatrienone is predicted to have the orthogonal-bent structure shown in Figure 4. Good agreement with experimental *B* and *C* rotational constants is found. A rather large discrepancy between theory and experiment is found for the I_a moment of inertia; however, there is a large experimental uncertainty associated with this quantity. Preliminary results for pentatetraenone and hexapentaenone suggest that distortion from linearity of the heavy-atom chain is a general feature of the cumulenones and that the preferred direction of the distortion alternates between planar and orthogonal.

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Registry No. **3**, 63766-91-6; **4**, 61244-93-7; **4**-*d*, 71546-35-5; **4**-d_2, 71546-36-6; $CH_2{=}C{=}C{=}C{=}C{=}O$, 87829-10-5; $CH_2{=}C{=}C{=}C{=}C{=}C{=}O$, 63766-92-7.

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