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# Concerning Bent Structures of Cumulenones

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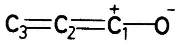
**Synopsis.** The cause of the unusual bent structures of cumulenones has been studied by HF/6-31G and MP3/6-31G methods. It is concluded that participation of the lone pair electrons to the adjacent $\pi$-bond results in the deformed structures.

Cumulenones ($CH_2{=}(C)_n{=}0$, $n$=0, 1, 2, ⋯) are topic compounds in practical and theoretical respects. Practically, they are potential candidates for interstelller compounds as those discovered for $n$=0 and 1.[1] It is an urgent requirement to establish those structures in order to assign unidentified microwave spectra of unidentified intersteller molecules. The structures of cumulenones have also aroused considerable theoretical interest[2] since an unusual bent structure has been determined for $n$=2.[3] A question arises as to what causes the distortion on the structures of cumulenones. We have studied this problem and have reached a very plausible explanation.

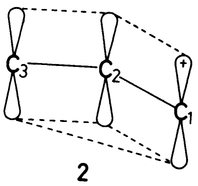
Recently, Farnell and Radom[2a] reported that the theoretically most stable structures of propadienone and butatrienone are planar-bent and orthogonal-bent structures, respectively. Such distortions from a $C_{2v}$ structure appear when the electron-correlation is included in the calculation. They also noted the results for the next members of the series, pentatetraenone ($CH_2(C)_4{=}0$) and hexapentaenone ($CH_2(C)_5{=}0$). Both of these molecules have been found to be bent even at the 4-31G[4] level.[2a] Thus, it seems that this bending of the carbon chain is a characteristic of cumulenones, alternating as a function of chain length between in-plane and out-of-plane structures.

There are two plausible reasons that can be considered from the organic chemistry of a carbonyl group, both of which are not well expressed in the Hartree-Fock theory. An oxygen atom has a larger electronegativity than a carbon atom. The withdrawal of a $\pi$-electron to the oxygen atom produces a cationic center on the carbon atom of the carbonyl group (**1**). Such a carbocation can interact with the $\beta$-carbon atom ($C_3$) in either a $\pi$ (**2**) or $\sigma$ (**3**) way. But, only the former interaction agrees with the observed bending direction.



$C_3{=}C_2{=}\overset{+}{C_1}{-}\overset{-}{O}$

1



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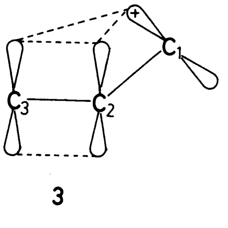

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The alternating contribution of a carbonyl group represents a participation of one pair of the lone-pair electrons of the oxygen atom into an adjacent $p$-atomic orbital (AO) or a $\pi$-bond (**4**). This resonance concept has been proposed by Brown *et al.* to explain the bent structure of propadienone.[3b] Such a contribution is regarded as a minor one from the point of view of the organic chemistry of a molecule. However, it often appears in ion chemistry as an acyl cation ($R\text{-}C{\equiv}O^+$). If this contribution takes place, the hybridization of the $\alpha$-carbon atom ($C_2$) may be changed toward $sp^2$. This also explains the observed bending characteristics of cumulenones. In order to determine which resonance structure contributes the most, we examined a series of cumulenyliums and cumulenides which are regarded as canonical structures of cumulenones.

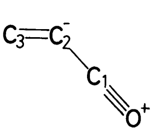

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Table 1 shows the relationship between the total energies and the bond angles of cumulenyliums and cumulenides (using the HF/6-31G[5] and MP3/6-31G method[6]). Optimization was carried out by HF/6-31G for all geometrical parameters except the fixed bond angle.[7] Table 2 shows the results of similar calculations regarding referential compounds. These can be compared with the ions listed in Table 1.

From Table 1, it can be seen that the most stable structure for cumulenylium has a $C_{2v}$ symmetry. Therefore, it should be understood that a cationic interaction does not make a major contribution to the distortion of cumulenone. Tables 1 and 2 indicate that a distortion of the bond by 10 degrees requires, by Hartree-Fock theory, only *ca.* 1 kcal/mol for both neutral molecules and cumulenyliums (either in-plane or out-of-plane). The existence of carbocation seems to have nothing to do with the flexibility. The inclusion of electron correlation reduces up to the half of such energy. This shows that cumulenyl groups are easily bent, although they look rigid according to the structural expressions of organic chemistry.

The $C_{2v}$ structures of cumulenides have higher total energies than those of specifically distorted structures. The optimized structures are largely deformed from the $C_{2v}$ symmetry and all have the Cs structures. The bending direction alternates as the number of carbon atoms increases, in accordance with the direction in cumulenones. Therefore, it is strongly suggested that the cause of a bent structure in cumulenones can be attributed to the participation of the lone-pair electrons. This theory can also explain why cumulenones with longer chains are apt to be deformed

Table 1. Relationship between total energies and bond angles in cumulenyliums and cumulenides[a)]

| | | | | in-plane | | | | | | out-of-plane | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\alpha$ | $\beta$ | $\gamma$ | HF/6-31G | MP2/6-31G | MP3/6-31G | $\alpha$ | $\beta$ | $\gamma$ | HF/6-31G | MP2/6-31G | MP3/6-31G |
| cation | | | | | | | | | | | | |
| $H_2C{=}\overset{\alpha}{C}{=}\overset{\beta}{C}\text{-}H$ | (180.0) | 180.0 | | −114.913119 | −115.154736 | −115.166638 | | | | | | |
| | (170.0) | 182.8 | | 1.0 | 0.4 | 0.5 | (170.0) | 179.9 | | 0.7 | 0.2 | 0.2 |
| | (160.0) | 186.1 | | 3.8 | 1.9 | 2.1 | (160.0) | 179.9 | | 2.6 | 1.3 | 1.2 |
| | | | | | | | (170.0) | | | | | |
| $H_2C{=}\overset{\gamma}{C}{=}\overset{\alpha}{C}{=}\overset{\beta}{C}\text{-}H$ | (180.0) | 180.0 | 180.0 | −152.749069 | −153.077903 | −153.089299 | | | | | | |
| | (170.0) | 180.0 | 179.9 | 0.7 | 0.2 | 0.0 | (170.0) | 182.1 | 180.0 | 1.0 | −0.1 | −0.1 |
| | (160.0) | 180.7 | 180.0 | 2.7 | 1.4 | 1.1 | (160.0) | 185.8 | 180.0 | 3.9 | 1.1 | 1.2 |
| anion | | | | | | | | | | | | |
| $H_2C{=}\overset{\alpha}{C}{=}\overset{\beta}{C}{=}H$ | (180.0) | (180.0) | | −115.154770 | −115.418316 | −115.429553 | | | | | | |
| | (170.0) | 183.2 | | 1.3 | 0.9 | 0.9 | (170.0) | 237.4 | | −4.0 | −6.1 | −6.7 |
| | (160.0) | 186.6 | | 5.0 | 3.7 | 3.7 | (160.0) | 238.0 | | −0.4 | −4.5 | −4.8 |
| optimized structure | | | | | | | 175.7 | 237.5 | | −115.162019 | −115.427657 | −115.440049 |
| $H_2C{=}\overset{\alpha}{C}{=}\overset{\beta}{C}{=}\overset{\gamma}{C}\text{-}H$ | (180.0) | (180.0) | (180.0) | −152.970564 | −153.316692 | −153.329619 | | | | | | |
| | (170.0) | 179.1 | 244.4 | −11.8 | −10.3 | −11.8 | (170.0) | 179.6 | 179.6 | 1.2 | 0.3 | 0.3 |
| | (160.0) | 180.8 | 242.6 | −11.1 | −11.1 | −12.2 | (160.0) | 179.2 | 179.2 | 4.9 | 2.5 | 2.5 |
| optimized structure | 178.6 | 176.9 | 245.1 | −152.989666 | −153.332544 | −153.348040 | | | | | | |
| $H_2C{=}\overset{\gamma}{C}{=}\overset{\alpha}{C}{=}\overset{\beta}{C}\text{-}H$ | (170.0) | 180.5 | 239.9 | −11.5 | −15.3 | −14.8 | (170.0) | 182.3 | (180.0) | 1.1 | 0.3 | 0.2 |
| | (160.0) | 187.5 | 239.4 | −9.0 | −14.4 | −13.7 | (160.0) | 185.2 | (180.0) | 4.4 | 2.8 | 2.6 |
| optimized structure | 174.3 | 178.4 | 240.3 | −152.989374 | −153.340916 | −153.353018 | | | | | | |

a) Values in parentheses are fixed bond angles. Other bond angles are optimized to the total energy with restriction of the fixed angles. Total energies are shown only for the optimized structures and the $C_{2v}$ structures. Other energies are expressed by the differences from those for the $C_{2v}$ structures in kcal/mol.

Table 2. Relationship between total energies and bond angles in neutral molecules

| | $\alpha$ | HF/6-31G | MP2/6-31G | MP3/6-31G |
|---|---|---|---|---|
| $CH_3\text{-}\overset{\alpha}{C}{\equiv}C\text{-}H$ | 180.0 | −115.823530 | −116.090768 | −116.103855 |
| | 170.0 | 1.1 | 0.4 | 0.5 |
| | 160.0 | 4.4 | 2.3 | 2.5 |
| $CH_2{=}\overset{\alpha}{C}{=}CH_2$ | 180.0 | −115.821517 | −116.081443 | −116.102218 |
| | 170.0 | 1.1 | 0.8 | 0.8 |
| | 160.0 | 4.6 | 3.3 | 3.2 |
| $CH_2{=}\overset{\alpha}{C}{=}O$ | | | | |
| in-plane | 180.0 | −151.649119 | −151.951174 | −151.946052 |
| | 170.0 | 1.5 | 1.1 | 4.3 |
| | 160.0 | 5.9 | 4.6 | 7.8 |
| out-of-plane | 170.0 | 1.5 | 1.1 | 4.3 |
| | 160.0 | 6.2 | 4.6 | 7.7 |

more easily: the contribution of the resonance structure **4** forms a negative charge on $C_2$. It is unstable in a short chain since the negative charge cannot be well delocalized.

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5) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).

6) The MP3/6-31G method represents that electron correlation is incorporated by the second and third-order Moller-Plesset perturbation theory (C. Moller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934)) using MO's obtained by the 6-31G method.

7) We have used the GAUSSIAN-80H program (Hitac Version of GAUSSIAN-80 (QCPE 437, 1982)) at the Computer Center of the University of Tokyo.