The Structure of Singlet Carbene Molecules

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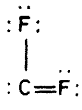
Summary Application of the principles of chemical bonding to the problem of the structure of singlet carbenes CX_2 leads to bent structures for $X = F$, OH, and NH_2, and linear structures for $X = Li$, BeH, and BH_2, in agreement with the *ab initio* calculations recently reported by Schoeller; these structures involve double bonds, with transfer of an electron from X to C for the first set and from C to X for the second, and the bond angle is determined by the availability of orbitals, not the electronegativity difference of C and X, which, however, helps to determine the stability of the carbene.

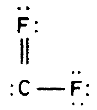
SCHOELLER[1] has reported the results of *ab initio* calculations with the STO-3G basis set of the normal-state geometry of the singlet carbenes CX_2 with X the unicovalent radicals involving atoms from Li to F. His conclusion is that these carbenes are linear if X is an element or group less electronegative (Li to B) than the central carbon atom and are bent if X is an element or group more electronegative (N to F) than the central carbon atom. Application to this problem of the principles of chemical bonding discussed in ref. 2 leads to the conclusion that it is not primarily the electronegativity but instead the number of available orbitals that determines the bond angle. Moreover, there are significant advantages to discussing the structures in terms of resonance between a single bond and a double bond rather than in terms of a two-electron three-centre bond, and also, for $X = Li$, BeH, or BH_2, as involving the p_y orbital of the carbon atom rather than the p_z orbital.

I discuss first the structure of singlet CH_2. There is a single bond to each hydrogen atom and the unshared electron pair occupies a third orbital in the *L* shell of the carbon atom. The three carbon orbitals may be described as sp^2 planar hybrids, but they are not equivalent because the greater stability of 2*s* than of 2*p* requires that the unshared-pair orbital, containing two electrons rather than one, have more *s* character than either of the two bond orbitals. A simple calculation[2a] for a similar problem (H_2O, NH_3, *etc.*) gives the result that the bond orbitals have about 5 or 6% *s* character (95 or 94% *p*), which corresponds to a bond angle of about 93°, as is observed for H_2S and other hydrides; the experimental values for H_2O (104·5°) and NH_3 (107·3°) are somewhat larger.



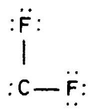
$\begin{array}{l} :\ddot{F}: \\ \;| \\ :C{=}\ddot{F}: \end{array}$

(A)



$\begin{array}{l} \;\;\ddot{F}: \\ \;\;\| \\ :C{-}\ddot{\underset{..}{F}}: \end{array}$

(B)



$\begin{array}{l} :\ddot{F}: \\ \;\;| \\ :C{-}\ddot{\underset{..}{F}}: \end{array}$

(C)

$Li{=}C{-}Li$ (D) $Li{-}C{=}Li$ (E) $Li{-}\ddot{C}{-}Li$ (F)

The structure of CF_2 is different, in that the fluorine atoms have extra electron pairs. One of these pairs can interact with the fourth orbital (p_z) of the carbon to form an additional covalent bond, so that the structures (A) and (B) as well as (C) can contribute to the normal state of this singlet carbene. The first two structures involve the transfer of an electron to the carbon atom, which is compatible with the principle of electroneutrality because of the 43% of ionic character of a C–F bond;[2b] the resultant charge on the carbon atom for either of the first two structures is +0·29, that for the third being +0·86. It is likely that the first two structures contribute more than the third. Similar resonance structures are expected for $C(OH)_2$ and $C(NH_2)_2$.

Table. Properties of singlet carbenes CX_2 from *ab initio* calculations.

X	∠XCX/°	r_{C-X}/Å	Single bond length/Å
F	102·8	1·323	1·385[a]
OH	101·9	1·354	1·431[a]
OCH_3	101·0	1·358	1·431[a]
NH_2	109·2	1·356	1·472[a]
H	100·2	1·127	1·094[b]
BH_2	180	1·419	1·56[a]
BeH	180	1·612	1·72[c]
Li	180	1·842	1·96[c]

[a] From alkyl derivatives. [b] From CH_4. [c] From covalent radii.

In the Table there are shown the calculated bond lengths for these three molecules and $C(OCH_3)_2$ and the values of the length of a single bond as observed in molecules such as H_3CF, H_3COH, and H_3CNH_2. The average difference is 0·082 Å, which corresponds[2c] to 36% contribution of each of the first two structures and 28% contribution of the third. The corresponding value of the bond angle (weighted average of 114° for each of the first two structures[2d] and 93° for the third) is 108°, in rough agreement with the average of the calculated values of ref. 1, 104°.

The molecules $C(BH_2)_2$, $C(BeH)_2$, and CLi_2 have a special feature, the availability of another stable orbital on the ligated atoms with which the unshared pair of the carbon atom can interact to form an additional covalent bond, giving structures such as (D) and (E) as well as (F). Lithium is less electronegative than carbon, the B–C bond having about 43% ionic character, which leads to −0·29 for the resultant charge on the carbon atom for the first two structures and −0·86 for the third. The average bond shortening for the three substances, rather uncertain because of uncertainty in the single-bond lengths, is 0·122 Å, close to the value for the first two structures, 0·110 Å. The bond angle for these structures is 180°. For all three structures the carbon atom can be described as sp^2, with the fourth orbital (p_z) empty. The double bond in the first two structures can be described as two bent single bonds in the σ plane.

The foregoing discussion provides a sound theoretical basis for the observation by Schoeller that elements more electronegative than carbon form bent carbenes and those less electronegative form linear carbenes. The linear carbenes are linear because a double bond is formed with use of the carbon electron pair, leaving the carbon atom with the formal charge +1. If the ligand atoms are more electronegative than the carbon atom the partial ionic character of the bonds tends to increase the charge on the carbon atom to more than +1, which is incompatible with the principle of electroneutrality.[2e] Similarly, groups such as PH_2 and AsH_2, with the central atom able to use one of its electron pairs to form a double bond with the carbon atom but with the wrong electronegativity, can be predicted not to form stable carbenes. If the compounds were to be stable enough to be studied, they would be found to be bent rather than linear, even though the ligands are less electronegative than carbon. The electronegativity difference is involved in determining the stability of the molecule, but the structure and the bond angle are determined by the available orbitals.

The description of these molecules as involving resonance of structures with single bonds and double bonds has, in my opinion, a significant advantage over the description in terms of a two-electron three-centre bond. Chemists know a great deal about the properties of single bonds and double bonds, and this knowledge can be used in the prediction of bond lengths and bond angles. The two-electron three-centre bond, on the other hand, constitutes a new structural feature that cannot be so easily incorporated into chemical structure theory.

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[1] W. W. Schoeller, *J. Chem. Soc., Chem. Commun.*, 1980, 124.

[2] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 3rd edn., 1960, (a), pp. 120—123; (b), pp. 93 and 98; (c), p. 237; (d), p. 141; (e), p. 172.