When is a Singlet Carbene Linear?

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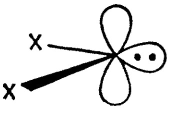
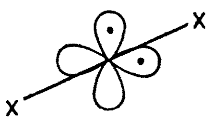
Summary Singlet carbenes CX_2 are linear if X are elements or groups less electronegative (Li to B) than the central carbon atom, and are bent if X are elements or groups more electronegative (N to F) than carbon

SINCE the discovery of methylene (**1**) (X = H) as a metastable intermediate[1] the scope of its reactivity has been widely explored [2] Here we present theoretical evidence that the common rule, that a singlet carbene is bent, is violated in favour of a linear conformation (**2**), if X are elements or atomic groups less electronegative than carbon

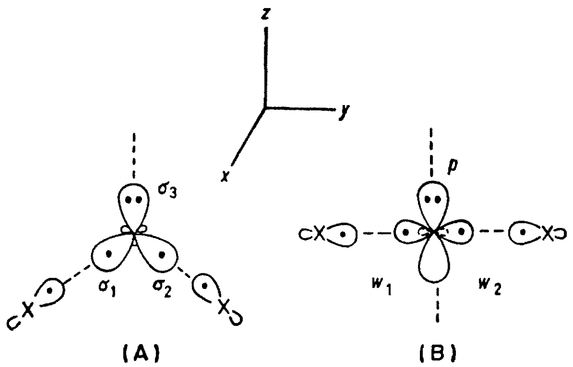


(**1**)



(**2**)

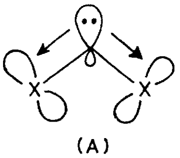
The carbene CX_2 can be considered as being composed from bond formation between a hybridized carbon atom and two atoms (or groups) X The carbon atom possesses 4 valence electrons which can be placed into the orbitals $2s$, $2p_x$, $2p_y$, and $2p_z$ Alternatively, these orbitals can be used to form a set of hybrid orbitals (i) In (A) three sp^2-hybrids (σ_1 to σ_3) and a perpendicular p-orbital (p_x) are constructed Two electrons are placed into the σ_3 orbital and two are used to form two-centre bonds with X This results in a singlet carbene with the configuration $^1(\sigma_3)^2$ (ii) In (B) the two sp-hybrids w_1 and w_2 are occupied by two electrons while the other two are placed into the orthogonal p_z (or p_x) orbitals This results in the singlet ground state configuration $1/\sqrt{2}\ \{(p_x)^2 - (p_z)^2\}$



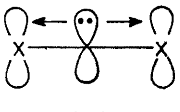
(A) (B)

Two extreme cases can now be differentiated

(i) If X is an element of the first to third group of the periodic table (*e g*, X = Li to B) it possesses empty p-orbitals which can form a stable two-electron three-centre bond with the orbital in the z-direction, σ_3 in (A) or p_z in (B) In (B) the two-electron three-centre bond is constituted by (a) through-space overlap between the atoms (groups) X



(A)



(B)

and (b) through-bond overlap between C and X. If the latter is more favourable the singlet carbene will adopt a linear conformation (B), alternatively a bent structure (A) will be preferred.[3]

Table. Geometry optimized *ab initio* calculations with the STO-3G basis set[a] for the singlet carbenes $:CX_2$ with X = Li to F.

X	r_{C-X}/Å	∠XCX/°
F	1·323	102·8
OH[b]	1·354	101·9
OMe[b]	1·358	101·0
NH_2	1·356	109·2
H	1·127	100·2
BH_2	1·419	180·0
BeH	1·612	180·0
Li	1·842	180·0

[a] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657. [b] All *trans* conformation.

(ii) Conversely, if X is an element of the fourth to seventh group of the periodic table (*e.g.*, X = Me to F) these (empty) *p*-orbitals are not available (*e.g.*, X = Me) or doubly occupied (*e.g.*, lone pairs in X = OMe, F). In this case a bent conformation (A) will be preferred, which is in agreement with the known bent structures of singlet carbenes.[2]

Our qualitative contention is supported by optimized *ab initio* calculations reported in the Table. For the singlet carbenes with X less electronegative than carbon they show the existence of a through-bond stabilized linear conformation (B) [case i(b)].

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[1] G. Herzberg and J. Shoosmith, *Nature*, 1959, **183**, 1801.

[2] 'Carbenes,' vols. I and II, eds. M. Jones and R. A. Moss, Wiley, New York, 1972.

[3] Two-electron three-centre bonding has also been invoked in discussions on planar tetraco-ordinate carbon; see R. Hoffmann, R. G. Alder, and C. F. Wilcox, *J. Amer. Chem. Soc.*, 1970, **92**, 4992; J. B. Collins, J. G. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *ibid.*, 1976, **98**, 5419.