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A THEORETICAL AB INITIO INVESTIGATION OF SUBSTITUTED ALKYLIDENE CARBENES

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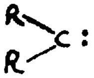
The carbene family can be divided into two major types: saturated carbenes 1, and unsaturated carbenes where the divalent carbon (carbenic center) is an integral part of an unsaturated system, as in the alkylidene carbenes 2.



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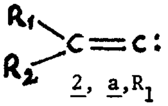
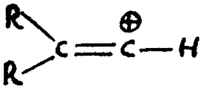


2, a, $R_1 = H$, $R_2 \neq H$
b, $R_1 = R_2 = H$



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In recent years, increasing attention has been given to unsaturated carbenes which provide a convenient route for the synthesis of small rings and other highly strained compounds.[1] The failure to observe unsaturated carbenes by direct spectroscopic methods, however, leaves these species poorly characterized. Very little is known for example about the effect of substituents on the geometries, the stabilities, or the singlet-triplet energy differences in unsaturated carbenes. Saturated carbenes have been studied extensively by theoreticians, but alkylidene carbenes have received little attention.[2] The parent $H_2C = C$[3a,b] and $F_2C = C$[3c] are the only alkylidene carbenes that have been studied by molecular orbital theory. The scarcity of reliable data regarding the most fundamental properties of alkylidene carbenes and the increasing interest in this field prompt us to study these species computationally.

This communication reports our calculations on a series of mono- and di-substituted alkylidene carbenes, 2a and 2b. We consider here only the singlet states, which we believe to be the ground states of these carbenes.[3,4] The substituents R are varied systematically along the whole series of the first short period substituents: Li, BeH, BH_2, CH_3, NH_2, OH, and F. This procedure, which was applied recently to carbenium ions,[5] allows us to quantitatively analyze the importance of the various properties of the β-substituent (such as σ-inductive effects, hyperconjugation, and π conjugation) in stabilizing the carbene. The substituents R = Cl, SiH_3 and CN, which are interesting experimentally, are also included. Calculations were carried out using the ab initio SCF-MO Gaussian 70 series of programs,[6a] using both the RHF/STO-3G[6b] and the RHF/4-31G[6c,d] methods. The monosubstituted carbenes (2a) were studied at standard geometries: r(C=C:) = 1.305 A°,[3b] r(=C-X) = standard,[7] $\angle XCC = \angle HCC = 120°$. These geometrical constraints were imposed for reasons discussed elsewhere,[5b] and because some of the carbenes may collapse on optimization to the corresponding bridged structures.[4] In order to elucidate substituents effects on the structure of the carbenes, we have studied the more symmetrical di-substituted carbenes (2b) which were optimized using the RHF/STO-3G method. The total energies of both 2a and 2b are presented in Table 1.

Table 1: Total energies of Mono- and Disubstituted Alkylidene Carbenes (2a and 2b), the Calculated Energies for Equations 1,2 and 3, and the Populations of the 2p-Carbenic Orbitals and the $2p(C^+)$ Orbitals.

Substituent	Energy,	hartrees	Calculated Energies for [i]			Mulliken Population of [m]	
			Eq.1 [j]	Eq.2 [k]	Eq.3 [j,l]		
(R=YHn)	2a(4-31G) [a]	2b(STO-3G) [b]	(4-31G)	(STO-3G)	(4-31G)	2p(C:)	$2p(C^+)$
H	- 76.65154 [b]	-75.78859	0.0	0.0	0.0	0.070	0.136
Li	- 83.53714	-89.34912 [f]	37.1	89.2	89.0	0.254	0.418
BeH	- 91.27762	-104.73667	18.5	46.9	26.4	0.166	0.263
Planar BH_2 [c]	101.88372	-125.72239	7.9	21.8	13.9	0.120	0.181
CH_3 [d]	-115.63170	-152.95764	- 0.9	0.4	10.9	0.076	0.141
Planar NH_2 [c]	-131.58168	-184.38831	-12.1	-15.9	5.4	0.047	0.080
OH [e]	-151.37035	-223.44359	-15.6	-11.5	-10.8	0.054	0.077
F	-175.34674	-270.68250	-19.0	-16.7	-32.0	0.045	0.076
CN	-168.23145	-256.87618	- 8.0	- 5.4	-	0.066	-
Cl	-535.03918 [g]	-983.77142	- 9.2 [g]	- 9.5	-	0.070	-
SiH_3	-362.58612 [h]	-649.38275 [a]	9.1 [h]	19.2 [j]	-	0.128	-

[a] Standard geometries. [b] Optimized geometries assuming C_{2v} symmetry and keeping the YHn bond lengths and bond angles at standard values. [c] The YH_2 group and YCC atoms lie in the same plane. [d] The HCC=C dihedral angle = 0°. [e] The HOCC dihedral angle = 0°. [f] Optimization was carried out keeping the LiCC angles at 120° as full optimization leads to the cyclic structure of dilithioacetylene; see: Y. Apeloig, P.v.R. Schleyer, J.S. Binkley, J.A. Pople, and W.L. Jorgensen, Tetrahedron Lett., 3923 (1976). [g] Using the 44-31G basis set, J.B.Collins, P.v.R. Schleyer, J.S. Binkley, and J.A. Pople, J. Chem. Phys. 64, 5142 (1976). [h] At RHF/STO-3G. [i] Using the energies of the most stable conformers for the carbenes (Table 1), the cations and the ethylenes. Energies of the mono- and disubstituted ethylenes from ref. 5 and 4 respectively. [j] All species except $H_2C = C$ at standard geometries. [k] All species except the ethylenes at optimized geometries. [l] From ref. 5b. [m] Number of electrons in the formally empty 2p orbital at the carbenic or the carbenium ion centers (STO-3G) of 2a and 3 respectively.

The stabilities of the substituted carbenes 2a and 2b are compared with that of the parent alkylidene carbene by means of the isodesmic reactions 1 and 2 respectively, and the results are summarized in Table 1. Table 1 also includes the calculated energies of the analogous reaction (eq. 3), which similarly compares the stabilities of β-substituted vinyl cations with that of the parent vinyl cation.[5b]

$$RHC = C: + H_2C = CH_2 \longrightarrow H_2C = C: + RHC = CH_2 \qquad (1)$$

$$R_2C = C: + H_2C = CH_2 \longrightarrow H_2C = C: + R_2C = CH_2 \qquad (2)$$

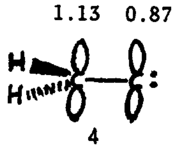
$$RHC = \overset{+}{C}H + H_2C = CH_2 \longrightarrow H_2C = \overset{+}{C}H + RHC = CH_2 \qquad (3)$$

It can be concluded from the data in Table 1 that electropositive substituents (relative to carbon) stabilize the carbene but electronegative substituents cause destabilization.

Similar results were obtained for the isoelectronic vinyl cations (eq. 3) and for the β - substituted ethyl cations.^{5b} This suggests^{5b} that σ-inductive electron donation and hyperconjugation (between the C–R bonding electrons and the empty carbenic 2p orbital) are the major stabilizing mechanisms for the alkylidene carbenes. The relative importance of these mechanisms cannot be deduced directly from our data but the importance of hyperconjugation can be demonstrated by examining the population of the formally empty 2p carbenic orbital (Table 1). This orbital is practically empty when R=F, but populated with 0.25 electrons when R=Li. Hyperconjugation also affects the carbene's structure; the C=C: bond length is shortened and the YC=C angle in 2b is narrowed as the substituent is changed along the series from fluorine (1.348Å, 123.7°) to more efficient hyperconjugating substituents such as beryllium (1.288 Å, 114.4°) or lithium(1.277Å).^{8}

The substituent effect is substantially smaller in the carbenes series (eq. 1) than in the vinylic cations series (eq. 3). The changing point from a stabilizing to a destabilizing substituent occurs earlier in the carbene series where methyl is slightly destabilizing. Although both species possess an empty 2p orbital, a larger substituent effect is expected in the carbenium ions which are positively charged and therefore exert a stronger electronic demand on the β-substituents. The reduced stabilization of the carbenes is also reflected in the lower population of the empty 2p orbital in 2a when compared to 3 (Table 1, columns 7 and 8). We note that an entirely different behavior is found in the saturated carbenes 1 where direct conjugation between the empty carbenic orbital and a lone pair of electrons on the substituent is possible. Thus, while NH_2 and F destabilize the alkydilene carbene, these substituents are highly stabilizing in 1.^{9} The large stabilizing effect which we predict for $R=SiH_3$ calls for experimental verification and points to possible preparative uses of such silylated alkylidene carbenes.

In addition to inductive effects and hyperconjugation, other mechanisms contribute to the total substituent effects in 2. A detailed analysis will be presented in a full paper, but one of these effects is discussed shortly here. We find that the π-electrons of the C=C bond are polarized in opposite directions in $H_2C=C$ and in $H_2C=\overset{+}{C}H$ (structures 4 and 5 respectively).



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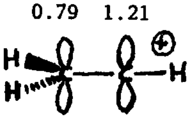

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The energetic consequence of this reversed polarization is nicely demonstrated by the following rigid rotation barriers around the =C-R bonds. For $R=BH_2$ the barrier (4-31G) is 11.3 kcal.mole^{-1} in the carbene 2a, 8.0 kcal. mole^{-1} in the ethylene $H_2BCH=CH_2$, but only 0.7 kcal. mole^{-1} in $H_2BCH=\overset{+}{C}H$. The opposite is found for $R=NH_2$ where the rotation barrier is the lowest in the carbene (0.1 kcal. mole^{-1}) intermediate in the ethylene (7.1 kcal. mole^{-1}) and the highest in the cation (10.9 kcal. mole^{-1}). It is therefore concluded that π-acceptors (e.g. $-BH_2$) are more effective and π-donors are less effective in stabilizing the carbene than in the corresponding ethylenes and vinyl cations. A further interesting result shows that the second substitution is uniformly more stabilizing than the first (compare reactions 1 and 2, Table 1). Two BeH or BH_2 substituents, for example, have a substantially larger stabilizing effect than a single substituent x 2. This effect is even more pronounced for electronegative substituents; two fluorines cause a combined destabilization of only 16.7 kcal. mole^{-1}, while a single fluorine destabilizes the carbene by 19 kcal. mole^{-1}.

We note that the calculated energies for eq. 1 with either the STO-3G or the 4-31G basis sets are very similar, and that geometry optimization of 2b results in small (1-5 kcal.mole^{-1}) energetic changes.[4] This shows that standard geometries and the STO-3G basis set can be used with some confidence for the study of singlet alkylidene carbenes. We are extending our studies to other substituents such as cyclopropyl, to the triplet states of 2, and to substituted vinylidene carbenes ($R_2C{=}C{=}C{:}$).

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References

1. For a recent review see: P.J. Stang, Chem. Rev., 78, August issue, in Press.
2. P.P. Gaspar and G.S. Hammond in "Carbenes," R.A. Moss and M. Jones, Jr., Ed., John Wiley & Sons, New York, 1975.
3. (a) J.H. Davis, W.A. Goddard 111, and L.B. Harding, J. Amer. Chem. Soc., 99, 2919 (1977); (b) W.A. Lathan, L.A. Curtiss, W.J. Hehre, J.B. Lisle, and J.A. Pople, Prog. Phys. Org. Chem., 11, 175 (1974); (c) O.P. Strausz, R.J. Norstrom, A.C. Hopkinson, M. Schoenborn, I.G. Csizmadia, Theoret. Chim. Acta, 29, 183 (1973).
4. Y. Apeloig and R. Schreiber, unpublished results.
5. (a) Y. Apeloig, P.v.R. Schleyer, and J.A. Pople, J. Amer. Chem. Soc., 99, 1291 (1977); (b) ibid, 5901 (1977).
6. (a) W.J. Hehre, W.A. Lathan, R. Ditchfield, M.D. Newton, and J.A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana;(b) W.J. Hehre, R.F. Stewart, and J.A. Pople, J. Chem. Phys., 51, 2657 (1969); (c) R. Ditchfield,W.J. Hehre, and J.A. Pople, ibid., 54, 724 (1971); (d) for lithium and beryllium the 5-21G basis set was used, J.D. Dill and J.A. Pople, ibid., 62, 2921 (1975).
7. (a) J.A. Pople and M.S. Gordon, J. Amer. Chem. Soc., 89, 4253 (1967); (b) J.D. Dill, P.v.R. Schleyer, and J.A. Pople, ibid., 98, 1663 (1976).
8. The full details of the optimized geometries of 2b will be presented in the full paper.
9. N.C. Baird and K.F. Taylor, J. Amer. Chem. Soc., 100, 1333 (1977).

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