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Sesquiacetylenes

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All-valence-electron SCF calculations support the linear "sesquiacetylenic" geometry in propargylic dianions. The two accompanying univalent cations are close to the central carbon, with an angle MC^2M of 90^0. The migration of lithium in allylic systems is interpreted as an intramolecular sigmatropic rearrangement.

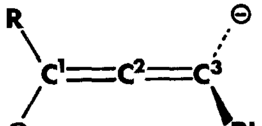
SCF-Rechnungen unter Benutzung aller Valenzelektronen stützen die lineare "sesquiacetylen"-ähnliche Geometrie in Propargyldianionen. Die beiden zugehörigen Kationen befinden sich in der Nähe des zentralen Kohlenstoffatoms und bilden einen MC^2M-Winkel von 90°. Die Wanderung des Lithiums in allylartigen Systemen wird als intramolekulare sigmatrope Umlagerung interpretiert.

Des calculs SCF pour tous les électrons de valence sont en faveur de la géométrie linéaire «sesquiacétylénique» dans les dianions propargyliques. Les deux cations univalents correspondants sont proches du carbone central avec un angle MC^2M de 90°. La migration du lithium dans les systèmes allyliques est interprétée comme un réarrangement intramoléculaire sigmatrope.

It has been shown [1–4] that two or more protons can be abstracted from a propargylic system ($RCH_2C{\equiv}CCH_2R$) and that this abstraction occurs preferentially on the same carbon [4], leading to $[RCH_2C{\equiv}CCR]^{-2}$ rather than to $[RCHC{\equiv}CCHR]^{-2}$. Also, in $PhC{\equiv}CCH_3$, the second proton is removed faster than the first, so that 1 mole of BuLi produces half a mole of dianion, no monoanion being detectable [4]. Furthermore [4], the NMR spectrum of $[RCH{=}CHCC{\equiv}CR]^{-2}$ shows that, unlike in monoanions, the charge is localized in the propargylic system. The phenomena were attributed to the stability of an eight-pi-electron system, when based on a linear, terminally substituted, three-carbon segment. The arrangement was termed [4] extended-acetylene or sesquiacetylene.

Here we report that SCF−MO calculations, of the CNDO/2-type [5], support the hypothesis of linearity and indicate that the sesquiacetylenic structure (*I*) is more stable than a twisted, allenic disposition (*II*). In these calculations, performed by a current [6] computer-program, we considered as


I


II

models several geometries of dianions derivable from propyne ($CH_3C{\equiv}CH$) and 2-butyne ($CH_3C{\equiv}CCH_3$). Geometrical details and computed energies are given in Tables 1 and 2. Despite certain limitations of the method [7], the energies are expected to reflect the order of stability of the various species.

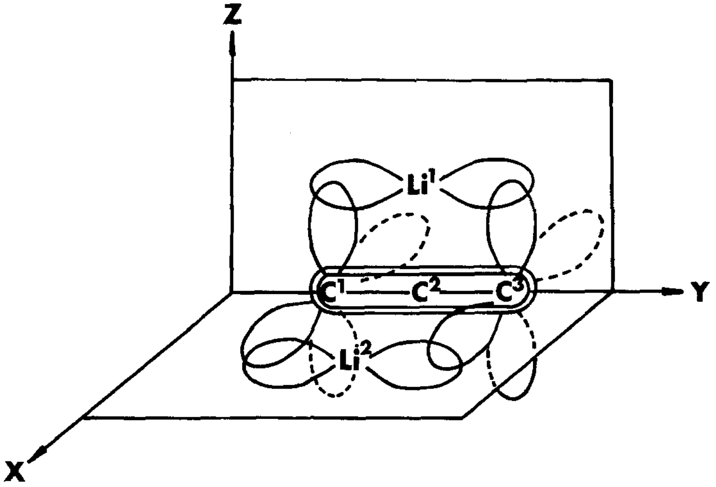
As for input geometries, both allenic and acetylenic bond-lengths, as well as intermediate situations, were examined; in the Tables, however, only results for *lowest-energy* structures are reported. For example, in the case of $C^1H_3C^2C^3C^4H$ (fifth species in Table 1), the energy was found to augment steadily as one passes from the acetylenic arrangement [$r(C^2C^3) = r(C^3C^4) = 1.20$ Å; $E = -843.04$ eV] to the allenic [$r(C^2C^3) = r(C^3C^4) = 1.31$ Å; $E = -838.56$ eV]. Also, at each value of r(CC), the stablest arrangement has $r(C^4H) = 1.08$ Å [values in the range 1.060 Å (allenic) to 1.096 Å (tetrahedral) were examined]. Accordingly, Table 1 reports only the case with $r(C^2C^3) = r(C^3C^4) = 1.20$ Å, $r(C^4H) = 1.08$ Å.

For the derivative of propyne ($[CHCCH]^{-2}$), a sesquiacetylenic linear structure, with equal CC-bond lengths, is found (Table 1) to be more stable, and to correspond to higher bond-populations, than any allenic arrangement; it is also endowed of a more pronounced charge-alternation. As for the Li atoms, it is seen (Table 2) that the optimal arrangement has them close to the central carbon (C^2), with an angle LiC^2Li of 90° (*III*); an angle of 180°, although characterized by a lower Li—Li repulsion, still corresponds to a higher total energy.

The two, almost degenerate, highest-occupied molecular orbitals have the following (overlap-renormalized) forms:

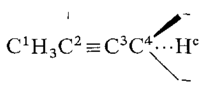
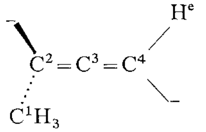
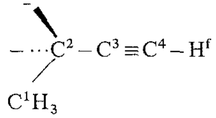
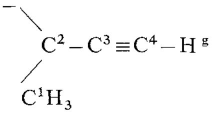
$$\varphi(\mathrm{HOMO}) = 0.4\,[x(C^1) - x(C^3) - z(C^1) + z(C^3)] + 0.3\,[y(\mathrm{Li}^1) + y(\mathrm{Li}^2)] + \cdots$$

$$\varphi(\mathrm{HOMO}-1) = 0.46\,[x(C^1) - x(C^3) + z(C^1) - z(C^3)] + 0.2\,[y(\mathrm{Li}^1) - y(\mathrm{Li}^2)] + \cdots$$



III

Table 1. CNDO/2 results for dianions

Dianion structure	Energy (eV)	Atomic population		Overlap population	
		Carbon	Hydrogen	CC	CH
I,[a] R′=R=H	−600.46	C^1, −0.905 C^2, +0.185	−0.188	1.506	0.788
I,[b] R′=R=H	−599.18	C^1, −0.852 C^2, +0.042	−0.169	1.419	0.790
II,[b] R′=R=H	−600.12	C^1, −0.776 C^2, −0.040	−0.204	1.209	0.547
 $C^1H_3C^2\equiv C^3C^4\cdots H^c$	−842.71	C^1, +0.146 C^2, −0.643 C^3, +0.115 C^4, −0.780	H^1, −0.220 H^4, −0.178	C^1C^2, 1.115 C^2C^3, 1.423 C^3C^4, 1.169	C^1H, 0.611 C^4H, 0.522
$C^1H_3C^2\equiv C^3-C^4-H^d$	−843.04	C^1, +0.176 C^2, −0.693 C^3, +0.182 C^4, −0.768	H^1, −0.244 H^4, −0.167	C^1C^2, 1.157 C^2C^3, 1.431 C^3C^4, 1.576	C^1H, 0.591 C^4H, 0.789
 $C^2=C^3=C^4$ H^e C^1H_3	−840.31	C^1, +0.163 C^2, −0.668 C^3, +0.032 C^4, −0.816	H^1, −0.211 H^4, −0.080	C^1C^2, 0.872 C^2C^3, 1.182 C^3C^4, 1.184	C^1H, 0.635 C^4H, 0.491
 $-\cdots C^2-C^3\equiv C^4-H^f$ C^1H_3	−838.92	C^1, +0.150 C^2, −0.909 C^3, −0.026 C^4, −0.455	H^1, −0.207 H^4, −0.138	C^1C^2, 0.784 C^2C^3, 0.904 C^3C^4, 1.583	C^1H, 0.643 C^4H, 0.797
 $C^2-C^3\equiv C^4-H^g$ C^1H_3	−840.91	C^1, +0.204 C^2, −0.745 C^3, +0.049 C^4, −0.592	H^1, −0.261 H^4, −0.133	C^1C^2, 0.921 C^2C^3, 0.869 C^3C^4, 1.633	C^1H, 0.583 C^4H, 0.796

[a] Distance $r(C^1C^2)=r(C^2C^3)=1.202$ Å, as in acetylenes [12, 13], $r(C^1H)=r(C^2H)=1.060$ Å, as in acetylene [14].

[b] $r(C^1C^2)=r(C^2C^3)=1.310$, $r(C^1H)=r(C^3H)=1.070$ Å, as in allene [13].

[c] $r(C^1C^2)=1.460$ Å as in propyne [12, 13], $r(C^2C^3)=r(C^3C^4)=1.203$ Å, $r(C^1H)=r(C^4H)=1.096$ Å [12]; C^1 and C^4 tetrahedral, with lone pairs occupying ligand positions.

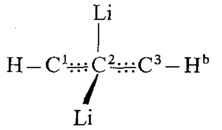
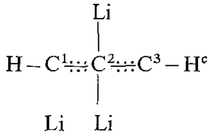
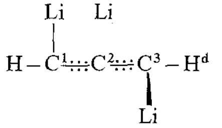
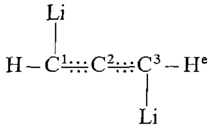
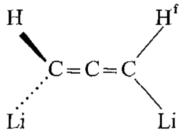
[d] $r(C^1C^2)=1.460$ [12, 13], $r(C^2C^3)=r(C^3C^4)=1.200$, $r(C^1H)=1.096$, $r(C^4H)=1.080$ Å [12]; C^1 tetrahedral, C^4 linear.

[e] $r(C^1C^2)=1.460$ [12, 13], $r(C^2C^3)=r(C^3C^4)=1.310$ as in allene [12], $r(C^1H)=1.096$, $r(C^4H)=1.080$Å [12]; C^2 and C^4 trigonal, with lone pairs occupying ligand positions.

[f] $r(C^1C^2)=1.540$ [14], $r(C^2C^3)=1.460$ [12, 13], $r(C^3C^4)=1.212$ [12], $r(C^1H)=1.096$ [12], $r(C^4H)=1.057$ Å as in acetylene [14]; C^2 tetrahedral, with lone pairs occupying ligand positions.

[g] As in *f*, but C^2 trigonal.

Table 2. CNDO/2 results for dilithio derivatives of propyne

Dilithio derivative[a]	Energy (eV)	Atomic population			Overlap population		
		Carbon	Lithium	Hydrogen	CC	CLi	CH
 [b]	-647.11	C^1, -0.481 C^2, $+0.217$	$+0.260$	$+0.112$	1.342	0.154	0.798
 [c]	-644.99	C^1, -0.586 C^2, $+0.202$	$+0.389$	$+0.097$	1.335	0.183	0.778
 [d]	-644.32	C^1, -0.492 C^2, $+0.237$	$+0.256$	$+0.118$	1.381	0.339	0.768
 [e]	-642.49	C^1, -0.601 C^2, $+0.023$	$+0.390$	$+0.096$	1.384	0.387	0.763
 [f]	-641.59	C^1, -0.439 C^2, $+0.103$	$+0.349$	$+0.039$	1.240	0.682	0.682

[a] The following were taken for all structures, except the last: $r(C^1C^2) = r(C^2C^3) = 1.202$ Å, as in acetylenes [12, 13], $r(CLi) = 2.2$ Å, as the shortest CLi-bond in solid CH_3Li [15] and CH_3CH_2Li [16], $r(CH) = 1.060$ Å [14], angle HCC of 180°. For the last (allenic): $r(C^1C^2) = r(C^2C^3) = 1.310$, $r(CH) = 1.070$ Å, as in allene [12], $r(CLi) = 2.2$ Å [15, 16], angle HCC of 120°.

[b] $LiC^2Li = 90°$.

[c] $LiC^2Li = 180°$.

[d] LiC^1C^3Li torsion angle 90°.

[e] LiC^1C^3Li torsion angle 180°.

[f] $HCLi = 120°$.

We note that the contribution of C^2 is here insignificant, and that electrons are distributed mainly in $2p_y$ orbitals of Li and in the perpendicular $2p_x$ and $2p_z$ of the terminal carbons. φ(HOMO) also corresponds to a pi-bond between the two Li-atoms. The lithium p_y bridges thus C^1 and C^3, while C^2 is in the MO node (*III*). Hence, incidentally, an explanation for the easy migration of Li in allylic systems [8–10], which we interpret as *intramolecular*, rather than intermolecular, and accompanied by inversion. It is thus an allowed [11] sigmatropic rearrangement.

The bond between the lithiums and C^2 evolves from deeper MO's and has some pi-character. This is illustrated by the following (last MO but one):

$$\varphi = 0.14\,[H^1 - H^2] + 0.46\,[s(C^1) - s(C^3)] \\ - 0.28\,y(C^2) - 0.07\,[y(Li^1) + y(Li^2)]\,.$$

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