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EXTENDED HUCKEL CALCULATIONS ON GROUP IV ALLYL COMPOUNDS EVIDENCE FOR σ-π CONJUGATION

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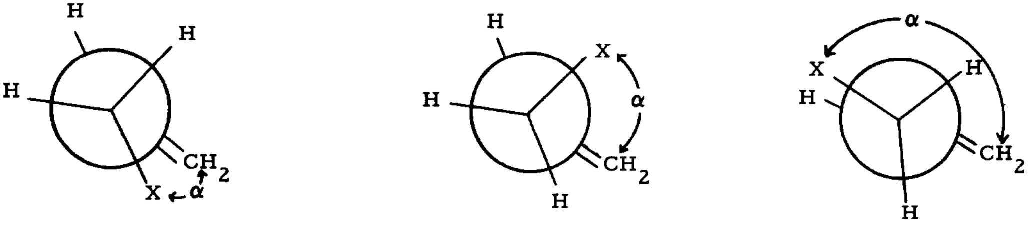
An allyl group bonded to a Group IV metal exhibits enhanced reactivity toward electrophilic reagents[1,2] and unusual spectral properties.[3] This atypical behavior has been cited as evidence for pπ-dπ bonding and σ-π carbon-metal hyperconjugation. A number of experimental[4] and theoretical[1,5] papers have recently provided convincing evidence for the importance of σ-π conjugation with allyl and benzyl organometallic compounds. We now report theoretical evidence for σ-π conjugation in a series of compounds containing an allyl group bonded to a Group IV metal atom (Fig. 1).



1, $\alpha = 0^\circ$

a) $X = C(CH_3)_3$
b) $X = Si(CH_3)_3$

2, $\alpha = 90^\circ$

c) $X = Ge(CH_3)_3$
d) $X = Sn(CH_3)_3$

3, $\alpha = 180^\circ$

e) $X = Pb(CH_3)_3$

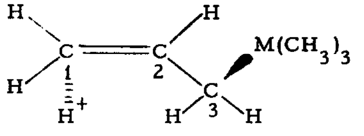
FIGURE 1

One of the first problems encountered in trying to assess the relative amounts of σ-π versus (d-p)π bonding in an allyl compound is the relative populations of the ground state conformers.[1] Extended Huckel[6] molecular orbital calculations suggest that all of the above compounds exhibit a shallow energy minimum at $\alpha \simeq 110$. In all cases the cis conformer **1** was considerably higher in energy than the trans conformer 3. The difference in total energy between 3a-3e and the lowest energy conformers ($\alpha \simeq 110^\circ$) ranged from 6.2 to 8.3 kcal/mole. These data suggest that those conformers which exist between the cis-gauche and the trans-gauche[1] and that favor σ-π conjugation would be most stable.

The σ-π conjugation effects should be maximized when the C_3-M σ bond is parallel to the π-orbitals of the C_1-C_2 double bond as in 2. Examination of the data in Table 1 indicates that the σ C-M bond is delocalized in the 90° conformation 2. Thus, in 2a-2e the approximate bond order of the double bond, based upon the Mulliken overlap population ($\rho_{C_1=C_2}$), decreases while the σ-π interaction of the π orbital on C_2 and the C-M σ bond is 2 also results in an increase in charge density at C_1 relative to the planar conformers 1 and 3. The increase in the polarizability of the C-M bond in 2b-2e is reflected in a decrease in the overlap population of the allyl carbon-M bond (ρ_{C_3-M}).

The EH calculations are also consistent with the experimentally observed spectral properties[3] and the decrease in the ionization potential[4,5] as a result of the σ-π conjugation. In the 90° configuration 2 the highest occupied molecular orbital is assigned to a linear combination of σ and π orbitals, resulting from σ-π delocalization. The HOMO in 1 and 3 is comprised largely of contributions from σ orbitals of the $-CH_2M(CH_3)_3$ moiety. The lowest unoccupied molecular orbital is assigned to the π^* orbital of the C_1-C_2 double bond. In all cases except carbon, the LUMO had slightly less π^* character in the 90° conformation than in the cis or trans conformation. In all cases the energy of the π orbital (E_π) was lower in the 90° conformation where σ-π mixing can occur.

Addition of a proton to the terminal carbon atom, as in 4, results in a marked increase in σ-π interaction and extensive perturbation of the carbon-carbon double bond ($\rho_{C_1=C_2}$). In all cases except 2a, $\rho_{\sigma-\pi}$ is considerably greater than the C_1-C_2 π overlap, ρ_π. Rehybridization at C_3 in 4 from sp^3 to sp^2 results in increased σ-π interaction but with an increase in energy.



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These results are therefore consistent with a vertical stabilization of 4 in the transition state, that does not require extensive heavy atom motion. In general, the charge on M increases (except for Pb) and ρ_{C_3-M} decreases as the C-M bond delocalizes to stabilize the neighboring cationic center. The extent of σ-π interaction is less for M=C than for the heavier atoms. Thus, the calculations adequately reflect the experimentally observed trends, despite the fact that d-orbitals have been omitted from the basis sets.[6]

TABLE 1

Charge Distributions and Overlap Populations

Compound	$Q^{a}_{C_1}$	Q^{b}_{M}	$\rho^{c}_{C_1=C_2}$	$\rho_{\pi_{C_1-C_2}}$	$\rho_{\sigma-\pi}$	ρ_{C_3-M}	$E^{d}_{\pi_{orb}}$	I. P.,[e] eV	LUMO[f]
1a	-0.089	0.135	1.387	0.520	0.010	0.754	-11.93	-11.12	-5.98
2a	-0.125	0.164	1.354	0.509	0.030	0.720	-12.49	-11.23	-5.96
3a	-0.107	0.140	1.352	0.513	-0.002	0.741	-12.26	-11.14	-6.18
1b	-0.111	1.222	1.378	0.514	0.010	0.681	-12.00	-10.94	-6.03
2b	-0.172	1.220	1.332	0.486	0.046	0.624	-12.29	-10.74	-5.77
3b	-0.102	1.198	1.360	0.514	-0.004	0.664	-12.17	-10.65	-6.24
1c	-0.110	1.208	1.368	0.512	0.010	0.661	-12.06	-11.08	-6.05
2c	-0.157	1.214	1.333	0.489	0.047	0.605	-12.29	-10.86	-5.88
3c	-0.101	1.188	1.358	0.513	-0.003	0.649	-12.16	-10.78	-6.25
1d	-0.106	1.357	1.367	0.510	0.010	0.640	-12.13	-11.14	-6.08
2d	-0.162	1.354	1.330	0.487	0.046	0.583	-12.27	-10.88	-5.87
3d	-0.100	1.328	1.359	0.513	-0.004	0.628	-12.16	-10.83	-6.26
1e	-0.103	1.359	1.365	0.510	0.010	0.626	-12.29	-11.19	-6.10
2e	-0.160	1.353	1.330	0.487	0.046	0.570	-12.27	-10.92	-5.89
3e	-0.100	1.327	1.359	0.513	-0.004	0.616	-12.16	-10.88	-6.26

[a] Net charge on the terminal carbon atom

[b] Net charge on M

[c] Mulliken overlap population, σ and π, for the $C_1=C_2$ double bond

[d] Energy of the molecular orbital comprised largely of π contributions from the double bond

[e] Calculated ionization potential assuming Koopmans' theorem; T. Koopmans, Physica, 1, 104 (1934)
The π contribution to HOMO in conformations 2a-2e was 25.4, 31.9, 31.0, 34.0 and 34.8%, respectively.

[f] Energy of the lowest unoccupied molecular orbital, eV

TABLE 2

EH Calculations on Protonated[a] Allyl Derivatives

Compound	Q_{C_1}	Q_M	$\rho_{C_1=C_2}$	$\rho_{\pi C_1-C_2}$	$\rho_{\sigma-\pi}$	ρ_{C_3-M}	I. P., ev
4a	0.109	0.213	1.016	0.192	0.124	0.671	-11.65
4b	0.081	1.262	0.979	0.154	0.187	0.543	-11.36
4c	0.086	1.264	0.983	0.161	0.178	0.518	-11.51
4d	0.084	1.402	0.980	0.159	0.180	0.494	-11.61
4e	0.085	1.402	0.981	0.160		0.481	-11.68

[a] The proton was added from the side opposite the substituent X ($\alpha = 90^\circ$) with a C_1-H^+ bond distance of 1.2Å and a bond angle of 90° relative to the nodal plane of the double bond.

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