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Preliminary communication

Theory and application of photoelectron spectroscopy
VII★. Through-conjugation through a tetrahedral silicon atom

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There is much current interest in physical properties of vinylsilanes[1]. A problem of considerable interest in these organosilicon compounds concerns the existence or non-existence of through-conjugation through the silicon atom in which d_π-orbitals form a π-electron bridge between otherwise independent π-systems (vinyl–Si–vinyl)[1]. We present below an argument that through-conjugation does, indeed, exist.

A previous study[2] on trimethylvinylsilane (I) has confirmed (i) that the HOMO★★ in (I) is the π-MO with a node between the ethylene π-MO and the $SiMe_3$ substituent, and (ii) that both Si–C hyperconjugation[3] and p_π–$d_\pi$bonding[1,4] are significant in determining the HOMO energy. The Si–C hyperconjugation raises the HOMO and p_π–d_π-bonding stabilizes it. The HOMO energy in (I), as measured by photoelectron spectroscopy, was 9.8 eV★★★. Next we investigated dimethyldivinylsilane, (II), and tetravinylsilane, (III), by the same method. The HOMO in (II) (C_{2v}- symmetry assumed) has one node between each Si–C= bond and is found at 9.8 eV. If D_{2d} symmetry is assumed for (III), we expect a degenerate pair of HOMO "π-MO's". Each MO is a mixture of a π-part (one node between each Si–C bond) on one divinyl system and a σ-part (mainly the antisymmetric combination of two Si–C MO's) on the other system. Here again, the HOMO energy is found to be 9.8 eV. Thus the HOMO energy is the same in all three compounds (I), (II) and (III).

In all three compounds the silicon atom is surrounded by four tetrahedral Si–C bonds, and thus the destabilizing Si–C hyperconjugation contribution to the HOMO energy in (I), (II) and (III) is expected to be constant. As shown previously, the p_π–d_π-bond in (I) bridges the node over the Si–C bond in the HOMO and thus stabilizes it. In (II) and (III) only one d_π-AO, which is directed along the C_2 axis, can contribute to the HOMO (within

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★ For Part VI see ref. 6.
★★ HOMO = highest occupied molecular orbital.
★★★ Measured by mass spectroscopy 9.8 eV [5]

the canonical set of MO's). This AO may be regarded as being built up by a linear combination of two d_π-AO's, each directed nearly along one Si–CH= bond. These d_π-AO's then bridge the node in each Si–CH= bond. The validity of this model of bonding (localized three-centre π-bonds) in a tetrahedral silicon atom bonded to more than one π-system is strongly supported by our observation from photoelectron spectroscopy, that the HOMO has the same energy in (I), (II) and (III). Thus through-conjugation (by p_π–d_π-bonding) through a tetrahedral silicon atom does indeed exist. In particular, the effects of d_π-conjugation in vinyl–Si and of d_π-through-conjugation in vinyl–Si–vinyl systems have the same magnitude.

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