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CNDO/2 CALCULATIONS CONCERNING THE GERMANIUM—CARBON DOUBLE BOND

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Summary

By suitable choice of parameters, the CNDO/2 method of calculation of molecular properties has been extended to include germanium atoms. Calculations have been made of energy-minimising bond lengths for germaethylene and fluorinated germaethylenes and of various properties of these optimised geometry models. These suggest that the germanium—carbon double bond would have somewhat unusual characteristics.

Introduction

Calculations have recently been published concerning the possible silaethylene molecule and some substituted derivatives. These have yielded information about likely molecular geometry [1,2], about charge distribution within the molecules [1,3] and about molecular force constants [2]. In these calculations, use has been made of extended Hückel [3], complete neglect of differential overlap (CNDO) [1,3] and ab initio [2] methods. Although the search for germaethylenes as products of reactions analogous to those in which the formation of silaethylenes is believed to occur has so far been unsuccessful [4], evidence for the formation of 2-ethyl-2-germabutene as an intermediate in the pyrolysis of the Diels—Alder adduct of germacyclohexadiene and perfluoro-2-butyne has recently been presented [5]. Since the search for such compounds might be helped by the availability of some model predictions of their likely properties, it was decided to attempt the calculation of some such properties by the CNDO/2 method, which would also permit comparison with the results of the similar calculations concerning silaethylenes.

The well-established CNDO/2 program [6] has accordingly been adapted to permit calculations concerning germanium atoms. Calculations have been made

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to ascertain optimum bond lengths, electron densities etc. for $H_2Ge{=}CH_2$, $H_2Ge{=}CF_2$, $F_2Ge{=}CH_2$ and $F_2Ge{=}CF_2$. The results indicate certain similarities with those described for the analogous silicon compounds, but also demonstrate some marked differences between the properties of silicon and germanium atoms in similar electronic environments.

Computational considerations

All calculations were made with a Burroughs B-5700 computer. The program used was based on that listed by Pople and Beveridge [6], adapted suitably for the Burroughs machine, the accuracy of the adaptation being verified by extensive comparison of results obtained with this version with those of calculations performed with the QCPE * version [7] on other machines.

As originally available, the CNDO/2 program is not parametrised for atoms beyond argon. Further adaptation was therefore required if it was to be used for calculations involving germanium atoms. This adaptation concerned the evaluation of the various overlap and Coulomb integrals and the selection of suitable Fock matrix parameters for germanium atoms.

The basis functions for the construction of the linear combinations of atomic orbitals in the original version are atomic wave functions obtained by Slater's prescription [8], where the dependence on the distance from the nucleus, r, is of the form $r^{n-1-\delta} \exp(-\zeta r)$, where n is the principal quantum number, δ is a parameter chosen to give best fit with experimental evidence and ζ is a parameter which takes into account the presence of other electrons and the value of the nuclear charge. The evaluation of the various integrals is straightforward when n is 1, 2 or 3 (for which values $\delta = 0$), but becomes unwieldy when n is 4 and δ 0.3, due to the presence of a non-integral exponent of r. Methods of overcoming this difficulty with the integrals have been discussed by Sichel and Whitehead [9], but the simplest is the use of atomic wave functions obtained by Burns' prescription [10], where by a different choice of ζ it is possible to avoid the need for a parameter corresponding to Slater's δ. Use of Burns' orbitals in CNDO calculations has been described by Brown et al. [11]. The use of Burns' orbitals does involve the introduction of different values of ζ depending on whether the wave function is one for an *s*, *p* or *d* electron, whereas the same value is used for all three types of Slater orbital, but the necessary adaptation of the program to accomodate this change is straightforward.

A further alteration is, however, necessary in order to permit extension of the program to deal with atoms with electrons with principal quantum number equal to 4. The subroutine for the evaluation of the various integrals makes use of the method described by Mulliken et al. [12] in conjunction with look-up tables for finding the various necessary coefficients. This subroutine was replaced by one based on that used by Brown et al. [11] where the various coefficients were calculated as required, since the extension of the tables to include all the additional information would be a major task. The validity of this amended subprogram for integral evaluation was verified by comparison of integrals obtained with it and those obtained with the original subprogram for a variety of selections of Slater

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* QCPE = Quantum Chemistry Programme Exchange.

orbitals. Thereafter Burns' orbitals were used for all the remaining calculations to be described. The interatomic Coulomb integrals were calculated using the appropriate *s* orbitals.

The establishment of the original Fock matrix in the CNDO/2 method depends on values of electronegativity for each orbital and of a bonding constant, β^0, for each atom. Values of these parameters for germanium atoms had to be selected before calculations could be performed. In the original parametrisation of the CNDO/2 program [13,14], the selection of the corresponding values was made in such a way that good agreement was obtained between the results of CNDO/2 calculations and others made by less approximate means. Since such more refined calculations are more time-consuming, and would be for this reason, if no other, essentially impracticable for more than a few germanium-containing species, an alternative approach to parameter selection was adopted.

Electronegativities for the 4*s* and 4*p* electrons were obtained from ionisation potentials and electron affinities calculated from the data given by Sichel and Whitehead [15]. For the 4*d* orbitals, a value of 0.1 eV, smaller than that for silicon 3*d* orbitals [14], was used. Calculations where this was replaced by values of 0.0 or 0.2 eV indicated that such changes had only a minor influence on the results.

The choice of the bonding parameter, β^0, was initially made by extrapolation of the values used by Segal et al. [13,14] for carbon and silicon atoms, whereby a value of —6.0 eV was obtained. This was also in apparent agreement with the values for germanium listed by Sichel and Whitehead [9], from which a value of around —4.5 eV would be expected to be certainly too high, since for the atoms for which comparison between the Segal parameters and those of Sichel and Whitehead's alternative computation can be made, the former are always more negative. Examination of the dependence of the results on the value of β^0 was made by setting this parameter alternatively to —2.0 and —10.0 eV. For calculations with germaethylenes containing carbon—hydrogen bonds all of the values gave reasonably similar results. However, in calculations with germaethylenes fluorinated on the carbon atom, convergence of the self-consistent field iterations could not be achieved when the value was —2.0 eV and was not always obtained with the value of —6.0 eV. Accordingly the value of —10.0 eV was finally adopted as the working value for β^0 for subsequent calculations. Possibly some value between this and —6.0 eV might arguably be more in agreement with expectation, but the dependence of the results, as distinct from their being obtainable at all, on the parametrisation was relatively slight, when compared with the likely inaccuracies present elsewhere in the CNDO/2 approximation.

The program finally used, therefore, was one in which Burns' atomic wave functions were used for all atoms, and the parameters for germanium were: β^0 = —10.0 eV; electronegativities for germanium valence shell orbitals (in eV), 4*s*, 12.716; 4*p*, 6.845; 4*d*, 0.1. The program also incorporated the evaluation of "valences" and bond indices are described by Armstrong et al. [16].

Calculations

A large number of calculations were performed with the program to test its reliability and to examine the effect of the change to Burns' orbitals on the results for calculations where Slater orbitals might also have been used. These indicated that the effect of the change was generally slight, at least when atoms of hydrogen, carbon, fluorine and silicon were considered, reasonable agreement between results for bond length optimisation with the different basis sets being obtained. Confidence in the suitability of this change was therefore gained.

Although the CNDO/2 method is possibly better for the calculation of bond angles than it is for finding bond lengths [12], the problem of making calculations concerning new types of bond, such as Ge=C, is mainly concerned with bond length. Pople and Gordon [17] have recommended that in comparative calculations a reasonably simple fixed geometry should be selected, since the advantages to be gained by taking into account changes in geometry from one molecule to another when replacement of atoms by other atoms of similar bonding occurs are probably outweighed by other factors. In their CNDO/2 results for silaethylenes, Damrauer and Williams [1] established that these molecules were planar and reported optimised bond angles of 120° for $H_2Si{=}CH_2$. More refined calculations [2] gave values of 122.9 and 122.7° for the H—Si—C and Si—C—H angles respectively, indicating that even in bond angle calculation the CNDO/2 method leaves something to be desired. In this work, therefore, it has been assumed that germaethylenes are planar with all bond angles 120°. Optimisation of bond lengths only to give minimum molecular energy has been attempted.

In order to obtain suitable starting values for exploration of the bond lengths in germaethylenes, calculations of the optimum bond lengths for CH_4, CF_4, GeH_4 and GeF_4 were made with the program described above. Simple variation of bond lengths, retaining T_d symmetry, gave results without difficulty. With these starting values, the optimisation in the case of the germaethylenes involved primarily optimisation of the Ge=C bond length, keeping the other bond lengths fixed, in order to obtain a reasonable approximation to the final value. Thereafter small variations in all the bond lengths were made, conserving C_{2v} symmetry throughout until final optimum sets of bond lengths were obtained. Although Damrauer and Williams [1] indicate that independent optimisation of the various bond lengths (and bond angles) gave the final optimum values for silaethylenes without further refinement, the results of the current set of calculations revealed that there was some slight interdependence of the various apparent optima, so that careful refinement was necessary to obtain optimum sets where variation of the length of any bond (preserving symmetry) by 1 pm caused an increase in the molecular energy.

Results and discussion

The preliminary calculations of optimum bond lengths for MX_4 species gave results of 124, 142, 155, and 171 pm for C—H, C—F, Ge—H and Ge—F bonds respectively. The results of the bond length optimisation calculations for the germaethylenes, together with other properties as calculated for the optimum bond-length sets, are given in Table 1.

Bond lengths

The calculated optimum bond lengths for the various germaethylenes show that, whilst there is some slight lengthening of the Ge=C bond when the atoms

TABLE 1

RESULTS OF CALCULATIONS FOR MOLECULES $X_2Ge{=}CY_2$

	$H_2Ge{=}CH_2$	$H_2Ge{=}CF_2$	$F_2Ge{=}CH_2$	$F_2Ge{=}CF_2$
Optimised bond lengths (pm)				
Ge=C	168	171	170	172
Ge—X	155	154	172	172
C—Y	125	140	124	140
Electron densities on atoms				
Ge	4.139	4.400	3.627	3.857
C	4.027	3.503	4.097	3.556
X	0.979	0.925	7.248	7.203
Y	0.938	7.123	0.890	7.091
Dipole moment in the sense $^{-}Ge{=}C^{+}$ (Debye)	1.021	1.222	3.347	3.425
Valences of atoms				
Ge	4.274	3.904	4.280	4.034
C	3.966	3.717	3.926	3.783
X	1.000	0.994	1.167	1.170
Y	0.996	1.261	0.988	1.276
Bond indices				
Ge—C	2.189	1.684	2.074	1.665
Ge—X	0.963	0.956	1.029	1.029
C—Y	0.887	1.011	0.883	1.015

attached to carbon are changed from hydrogen to fluorine, this is much less marked than the corresponding change reported for silaethylenes [1]. The lengths of the single bonds between germanium or carbon and hydrogen or fluorine are close to those found for the simple MX_4 species in the preliminary calculations. These observations suggest that the formation of the germanium—carbon double bond has little effect on the other bonding properties of the two atoms involved and that there is less influence by the other bonds on these atoms than is found in the silaethylenes.

Electron densities and dipole moments

With the exception of $F_2Ge{=}CH_2$, the electron density calculated for the germanium atom in the germaethylenes is always greater than for the carbon atom, so that the polarity of the Ge=C bond is in the sense $^{-}Ge{=}C^{+}$. In the exceptional case, the difference may be attributed to electron withdrawal from the germanium towards the fluorine atoms, a phenomenon which seems to have been transmitted even to the hydrogen atoms from which some electron withdrawal seems to have occurred. The polarity of the Ge=C bond seems therefore to be opposite to that found for the Si=C bond [1,2]. This gives some support to the concept of alternation of electronegativity from atom to atom in Group IV [18].

The values for the dipole moments calculated for the set of germaethylenes indicate that the influence of the presence of fluorine attached to the germanium atom is the most significant effect apparent in the results, which is not surprising in view of the general polarity of the Ge=C bond. Replacement of hydrogen on the carbon by fluorine has only a slight effect on the dipole moment: this effect, however, is to increase the dipole moment in the "unexpected" sense, the change in the contribution from the *s*, *p* orbital rearrangement being more than sufficient to cancel out that due to the small alteration in charge distribution. The value for germaethylene is considerably smaller than that for silaethylene (at a non-optimised geometry) calculated by Curtis [2], suggesting that the Ge=C bond is rather less strongly polar than is the Si=C one. Values for the dipole moments of the various silaethylenes calculated for Damrauer and Wilsons optimised bond lengths [1] but with 120° angles, using Slater orbitals as basis functions, are, for $H_2Si=CH_2$, $H_2Si=CF_2$, $F_2Si=CH$ and $F_2Si=CF_2$ respectively, 2.226, 4.085, 0.109 and 2.335 Debye, all in the sense $^+Si=C^-$. In these there is a more obvious effect due to fluorine substitution for hydrogen on the carbon atom, which is due to the much greater change in the charge distribution which occurs in these molecules compared with the germaethylenes.

Valences and bond indices

The calculations of valences and bond indices from the density matrices obtained from CNDO/2 calculations [16] is a recent attempt to obtain from these sets of figures numbers which may be meaningful to the chemist. Whilst there is some uncertainty as to whether the figures are fortuitously close to the values which the chemist might expect for simple bonding systems or have some deeper significance, their values may throw some additional light on the nature of bonding etc.

The calculated valences reveal a relatively marked change in most cases where fluorine substitution occurs. When fluorine replaces hydrogen on the germanium atom, the valence of this atom is slightly increased. When the replacement concerns the atoms attached to the carbon, a much more significant decrease in the valence of this atom is apparent together with some decrease in the valence of the germanium atom. These results suggest that, as expected, fluorine substitution withdraws electrons into the M—F bonds to such an extent that the availability of electrons for other bonding purposes is diminished, the effect being more marked in the case of carbon, possibly as a consequence of some back-donation of the electrons in the Ge—F case involving the significant use of *d* orbitals in both σ and π bonding with fluorine lone pairs.

The bond index results support these conclusions. The Ge=C bond index is markedly decreased when fluorine is substituted for hydrogen on the carbon atom. In all cases the indices of M—F bonds are greater than 1 implying some concentration of bonding electrons in excess of that which would give a simple single bond. Similarly the indices for M—H bonds are always somewhat less than unity, particularly for the C—H bonds, where the involvement of the carbon electrons in the formation of the "double" bond with germanium makes the bond to hydrogen somewhat weaker as a result.

Bond orders

The partial and total σ and π bond orders for the Ge—C bond are given in Table 2. Consideration of the total bond orders indicates that in all cases the π bond order is much greater than the σ one, and that extensive involvement of *d* orbitals is evident in both cases. There is considerable speculation concerning the role of *d* orbitals in the formation of π bonds, but their significance in rela-

TABLE 2

CALCULATED Ge—C BOND ORDER COMPONENTS

	$H_2Ge{=}CH_2$	$H_2Ge{=}CF_2$	$F_2Ge{=}CH_2$	$F_2Ge{=}CF_2$
$s\sigma$—$s\sigma$ bond order	0.334	0.358	0.343	0.386
$s\sigma$—$p\sigma$ bond order	—0.603	—0.466	—0.644	—0.508
$p\sigma$—$s\sigma$ bond order	0.538	0.598	0.489	0.541
$p\sigma$—$p\sigma$ bond order	—0.254	—0.285	—0.216	—0.279
$d\sigma$—$s\sigma$ bond order	0.053	0.078	0.040	0.490
$d\sigma$—$p\sigma$ bond order	0.272	0.082	0.324	0.131
Total σ bond order	0.341	0.366	0.336	0.220
$p\pi$—$p\pi$ bond order	0.947	0.828	0.870	0.822
$d\pi$—$p\pi$ bond order	0.308	0.179	0.405	0.253
Total π bond order	1.255	1.007	1.275	1.074

tion to the formation of σ bonds is often overlooked. Simple group theory consideration of the selection of atomic orbitals for the formation of trigonal bonds reveals that the σ bonds may involve not only the *s* and two of the *p* orbitals, but also three of the *d* orbitals, as is found to be the case here. The most significant changes on substitution of fluorine for hydrogen seem to occur when this takes place at the carbon atom, and are evident in both the σ and the π bond order contributions due to interaction of *p* and *d* electrons. It thus appears that fluorination at the carbon atom causes marked transference of electrons to the C—F bonds, and that these bonds have considerable π bond character. Indeed in the cases where the Ge—X bonds are to hydrogen, fluorination at the carbon causes some increase in the σ component of the Ge—C bond.

Conclusions

The results of the CNDO/2 calculations indicate that the germanium—carbon bond in germaethylenes has a somewhat unusual double-bond like character, in that it appears to consist of a relatively weak σ bond and a much stronger π bond. Both of these components involve significant use of the germanium *d* orbitals. The charge distribution is such that, when identical atoms are attached to the carbon and the germanium ends, the carbon end is positively charged compared with the other. Replacement of hydrogen by fluorine on the germanium has little effect on the majority of properties of the molecules, but the corresponding substitution at the carbon atom causes some weakening of the bond due to withdrawal of electrons to form σ and π bonds with the fluorine. This weakening is not, however, accompanied by any significant alteration in the bond length.

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