Journal of Organometallic Chemistry, 140 (1977) 265—272
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A CNDO/2 LOCALISED ORBITAL STUDY OF DIPOLE MOMENTS OF SILA- AND GERMA-ETHYLENES

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(Received May 30th, 1977)

Summary

CNDO/2 calculations have been performed to predict dipole moments for silaethylenes, with either Slater or Burns atomic orbitals, and for germaethylenes with Burns orbitals only. Trends on replacement of two hydrogen atoms at either end of the double bond by fluorine are similar in both sets for the silaethylenes and in accordance with expectation, but an anomalous trend is observed for fluorination of the carbon in germaethylenes.

Localised orbitals have been examined to seek an explanation for this anomaly. In all cases the trends are in the unexpected sense for the π orbitals but in the expected sense for the others taken together and for most of these individually. The anomaly with the germaethylenes thus appears to be associated with the relative magnitudes of these opposing trends, where donation of electrons via the π bond to the germanium atom outweighs the accumulation of charge around the fluorine atoms attached to the carbon.

Recently [1] we reported the results of some CNDO/2 calculations concerning germaethylenes, a notable feature in which was the influence on the dipole moment of substitution of fluorine for hydrogen at the carbon end of the molecule, where the effect was in the unexpected direction. The advantages of the use of localised orbitals, rather than the delocalised ones obtained by conventional CNDO/2 calculations, in ascribing dipole moments to features of the molecule recognisable to the chemist having been demonstrated by Kuznesof et al. [2], it was decided to apply their procedures to the germaethylene systems in an attempt to obtain further understanding of this strange phenomenon.

The parametrisation of the CNDO/2 method [3] for germanium, incorporating the use of Burns orbitals [4] for all atoms, was as previously described [1]. Localisation of the orbitals was achieved by a modification of the Edmiston—Ruedenberg method [5], bearing in mind the simplifications associated with the CNDO approximation pointed out by Trindle and Sinanoğlu [6], which has been published elsewhere [7]. Charge density and atomic polarisation dipole moment components were then obtained for each of the localised orbitals.

The orbital charge densities were obtained by the method described by Kuznesof et al. [2]. The coefficients of the atomic orbital contributions to each of the localised orbitals were examined to ascertain whether the orbital was a bond or a lone pair. Assuming an even distribution of the electrons giving a pair to each of the normalised localised orbitals, the pair was then assigned to the bonding atoms or lone pair atom as appropriate and the departure from this idealised situation calculated as the charge density component of the dipole moment for the orbital.

An oversight was detected in the earlier method used to calculate the atomic polarisation components of the dipole moments. This constituted the neglect of the difference in ζ values associated with *s*, *p* and *d* orbitals on any atom in the Burns approximation. The original calculations were made, as in the standard version of the CNDO/2 method [8], with a single ζ value for each atom. Using the terminology of Santry and Segal [9], the Burns orbitals constitute an *sp'd''* basis, but for the atomic polarisation calculations an effective *spd* basis was used.

The use of a basis other than *spd* in the CNDO method is possible only if some comprimise is made. Santry and Segal [9] used an *spd'* basis to examine the influence of the *d* orbital parametrisation on the results obtained with second row elements and in so doing sacrificed the desired independence of the results on the choice of hybrid basis sets by using different Coulomb integrals and derived nuclear attraction integrals depending on the natures of the atomic orbitals involved. In this work, as in that reported earlier [1], the alternative compromise of using Coulomb integrals obtained with the value of ζ appropriate for an *s* orbital, thus preserving the independence of the results on the nature of the basis set, was chosen. However, since it is possible to introduce the components of the *sp'd''* basis set explicitly into the formulae for the atomic polarisation dipole moment components, by slight extension of the formulae given by Santry and Segal for their *spd'* basis, this change, which would make the fullest practicable use of the properties of the basis set, was introduced.

Either of the atomic polarisation dipole moment components may be represented as the product of three terms: $\mu = abc$, where a is constant for a particular pair of orbital types (*sp* or *pd*), b is a term involving the quantum number and exponents of the orbitals concerned and c incorporates various of the atomic orbital coefficients present in the molecular orbitals, perhaps combined in the form of density matrix elements. The factor b can be given in general terms as

$$b = \frac{(n_1 + n_2 + 1) \cdot (\zeta_1 \zeta_2)^{\frac{1}{2}(n_1 + n_2 + 1)}}{2(\zeta_1 + \zeta_2)^{(n_1 + n_2 + 2)}}$$

where ζ_1 and ζ_2 are the appropriate values for the atomic orbitals involved, the principal quantum numbers of which are n_1, n_2, respectively.

If the coordinate system is aligned so that only the x components, say, of the dipole moments are of interest, then the atomic polarisation contributions for a given atom arising from a particular molecular orbital (whether localised or not) may be given in terms of the coefficients of the several atomic orbitals of the atom concerned in the molecular orbital selected, c_i, as follows:

$$\mu_x{}^{sp} = -2.(3)^{-1/2} \cdot b \cdot c_s \cdot c_{p_x}$$

and $\mu_x{}^{pd} = -2 \times (5)^{-1/2} \cdot b(c_{p_y}c_{d_{xy}} + c_{p_z}c_{d_{xz}} + c_{p_x}(c_{d_{x^2-y^2}} - (3)^{-1/2}c_{d_{z^2}}))$

By suitable summation of these (and the analogous y and z components if necessary) over all atoms and over all occupied orbitals, total contributions due to the atomic polarisations can be found. With an *spd* basis of Slater orbitals, results identical with those obtained with the standard program [8], which uses density matrix elements and factors b obtained by an appropriately simplified expression, were obtained for a variety of systems, confirming the accuracy of the computational procedure. The trend in the dipole moments of germaethylenes was found to be the same whether these were calculated using a single ζ value or the full *sp'd"* basis set.

Since it was possible that the trend was due to some property of the Burns orbitals, parallel calculations on the corresponding silaethylenes, where both Slater and Burns orbitals might be used, were performed. The trends there were unaltered in direction. Comparison of the two methods for calculation of the dipole moment when Burns orbitals were used was also made. An opportunity was taken in the single ζ calculations for the germaethylenes to correct an arithmetical error which was present in the earlier work.

Calculations were made on the IBM 370/165 at the University of Cambridge Computing Centre. This faster, more powerful machine permitted the use of less lax criteria for convergence than had been found convenient with the Burroughs machine on which the earlier calculations were made: this change produced some alteration in the calculated electron densities, which are somewhat sensitive to the extent of convergence of the SCF iteration stage.

The geometries used for the germaethylenes were as reported previously [1]. For the silaethylenes, the CNDO/2 optimised geometries given by Damrauer and Williams [10] were used. Fresh optimisation was not performed when the change to Burns orbitals was made, since this would have introduced a new feature requiring consideration. Although an alternative optimised planar geometry for silaethylene has been reported by Schlegel et al. [11], who also give a value for the dipole moment calculated by an abinitio method, this was not used since corresponding data for the other silaethylenes was not available. For similar reasons the non-planar geometry obtained from ab initio studies by Strausz et al. [12] was not used.

The total dipole moments for the various molecules calculated by the several different methods are given in Table 1. Here it is evident that the effect of replacing hydrogen on the carbon by fluorine is to decrease the dipole moment (in the sense $^-$M=C$^+$) for the silaethylenes, in accordance with expectation for the addition of an electronegative atom, but to increase it for the germaethylenes. These trends are independent of the particular set of basis functions used and of the method adopted for the calculation of the dipole moments. The anomaly previously recognised in the results for germaethylenes is thus further substantiated.

The change from Slater to Burns orbitals has, on the face of it, a marked effect

TABLE 1

CALCULATED DIPOLE MOMENTS FOR SILA- AND GERMA-ETHYLENES
(Dipole moments in the sense $^{-}M{=}C^{+}$. Values in Debyes)

	$H_2M{=}CH_2$	$H_2M{=}CF_2$	$F_2M{=}CH_2$	$F_2M{=}CF_2$
M = Si				
Slater orbitals	−2.226	−4.085	−0.110	−2.335
Burns orbitals - *sp'd"* [a]	1.027	0.284	2.154	0.365
Burns orbitals - single-ζ [a]	1.094	0.338	2.390	0.647
M = Ge				
Burns orbitals - *sp'd"* [a]	1.086	1.838	2.173	2.848
Burns orbitals - single-ζ [a]	1.062	1.795	2.036	2.670

[a] *sp'd"* and single-ζ refer to the different methods for calculating the dipole moments, see text.

on the results for the silaethylenes, but the trends on substitution remain unaltered. It is interesting to note that the value for the dipole moment for silaethylene obtained with Burns orbitals and the *sp'd"* method for calculating the final results is numerically in good agreement with the 1.1 D quoted by Schlegel et al. [11], although their comment on its direction suggests that in the present scheme a value of —1.1 D would have to be obtained to correspond with their ab initio results.

The results also show relatively little dependence on whether the dipole moments are calculated using the distinct ζ values of the Burns *sp'd"* basis or the single ζ value corresponding to a *s* orbital in all cases. The change from the *sp'd"* method to the single-ζ one causes a slight increase in the results for all the silaethylenes but a slight decrease for all the germaethylenes.

A breakdown of the various dipole moments into charge density and atomic polarisation components is given in Table 2. As with the total dipole moments, the effect of changing the method of calculation, when Burns orbitals are used, from that involving the full characteristics of the *sp'd"* basis to the single-ζ one is relatively slight. Such a change has, of course, no effect on the charge density components and, from the relative magnitudes of the ζ values concerned would be expected to have a greater effect on the *pd* polarisation components than on the *sp* ones. This expectation is borne out by the changes observed, the average alteration in the *sp* polarisation components being, for silaethylenes and germaethylenes respectively, —0.017 and —0.033 D while for the *pd* polarisation components the corresponding figures are +0.172 (Si) and —0.071 D (Ge). The total influence of the change in the method of calculation is thus associated in sign with that occurring in the *pd* polarisation moment components. Since the influence of the method of calculation of the dipole moments is so slight, further discussion will be limited to the results obtained by the *sp'd"* method.

From examination of the results in Table 2, it is evident that for some of the components the trend on substitution is to match that of the total values while for some of the others the opposite trend occurs. With some components no clear trend on substitution can be recognised. The overall trends are thus the results of the summation of opposing, rather than totally parallel effects. If we assume that our intuitive ideas concerning the addition of electronegative fluorine atoms are correct, so that replacement of hydrogen attached to carbon should

TABLE 2

CHARGE DENSITY AND ATOMIC POLARISATION COMPONENTS OF DIPOLE MOMENTS OF SILA- AND GERMA-ETHYLENES

(Dipole Moments in the sense $^{-}M{=}C^{+}$. Values in Debyes)

	$H_2M{=}CH_2$	$H_2M{=}CF_2$	$F_2M{=}CH_2$	$F_2M{=}CF_2$
M = Si				
Slater Orbitals				
Charge densities	0.052	−2.046	2.579	0.315
sp polarisation	0.173	0.503	−1.006	−0.806
pd polarisation	−2.452	−2.541	−1.682	−1.844
Burns Orbitals - sp′d″ [a]				
Charge densities	1.349	0.252	4.188	2.720
sp polarisation	0.278	0.930	−0.610	−0.363
pd polarisation	−0.600	−0.899	−1.423	−1.992
Burns orbitals - single-ζ [a]				
Charge densities	1.349	0.252	4.188	2.720
sp polarisation	0.262	0.859	−0.573	−0.359
pd polarisation	−0.516	−0.773	−1.224	−1.713
M = Ge				
Burns orbitals - sp′d″ [a]				
Charge densities	1.037	0.628	3.581	3.166
sp polarisation	0.231	1.338	−0.565	0.600
pd polarisation	−0.182	−0.129	−0.844	−0.917
Burns orbitals - single-ζ [a]				
Charge Densities	1.037	0.628	3.581	3.166
sp polarisation	0.232	1.312	−0.586	0.547
pd polarisation	−0.207	−0.146	−0.959	−1.042

[a] *Sp′d″* and single-ζ refer to the different methods for calculating the dipole moments see text.

decrease the dipole moment while replacement at the other end of the double bond should increase it, then this predicted trend is exhibited by the following components: (a) for silaethylenes with Slater orbitals: charge density and *pd* polarisation; (b) for silaethylenes with Burns orbitals: charge density; (c) for germaethylenes: charge density. The opposite trend for both substitutions is shown by the *sp* polarisation components in all cases. The *pd* polarisation components with Burns orbitals show no clear trend.

Consideration of the trends in the components is not therefore particularly helpful in ascribing an explanation to the anomalous overall effect observed in the results for the germaethylenes. It is at this stage, therefore, necessary to look at the contributions due to the various types of orbital to see whether some pattern can be recognised there which will afford an explanation. Here the use of localised orbitals, which permit the association of dipole moment components with chemically recognisable features of the electron arrangement of the molecules is particularly helpful.

In Tables 3, 4 and 5 are given the contributions to the dipole moments of the silaethylenes (with both Slater and Burns orbitals) and germaethylenes due to the several distinct types of localised orbitals. The figures represent, in each case, the component of the appropriate orbital dipole moment aligned with the M—C axis. Examination of these results reveals that the most marked trend in the direction opposite to our earlier assumption is found in the charge density components

TABLE 3

LOCALISED ORBITAL CONTRIBUTIONS TO DIPOLE MOMENTS OF SILAETHYLENES $X_2Si=CY_2$
(Slater orbitals. Dipole moments in the sense $^-Si=C^+$. Values in D)

	$H_2Si=CH_2$	$H_2Si=CF_2$	$F_2Si=CH_2$	$F_2Si=CF_2$
Charge densities				
Si—C σ bond	−0.726	−1.961	−0.007	−1.158
Si—C π bond	−2.086	−0.469	−2.962	−1.397
Si—X bond	0.431	0.255	2.687	2.574
C—Y bond	1.001	−0.588	1.114	−0.450
X lone pairs			−1.163	−1.201
Y lone pairs		0.524		0.511
sp atomic polarisations				
Si—C σ bond	−0.620	0.218	−1.031	−0.328
Si—C π bond	0	0	0	0
Si—X bond	1.552	1.556	−0.287	−0.226
C—Y bond	−1.156	−0.023	−1.129	−0.052
X lone pairs			1.428	1.428
Y lone pairs		−1.391		−1.389
pd atomic polarisations				
Si—C σ bond	−1.224	−1.246	−0.919	−1.000
Si—C π bond	−2.134	−2.488	−1.943	−2.305
Si—X bond	0.675	0.690	0.516	0.522
C—Y bond	−0.221	−0.054	−0.256	−0.071
X lone pairs			0.330	0.326
Y lone pairs		−0.039		−0.046

TABLE 4

LOCALISED ORBITAL CONTRIBUTIONS TO DIPOLE MOMENTS OF SILAETHYLENES $X_2Si=CY_2$
(Burns orbitals. $sp^{\prime}d^{\prime\prime}$ method for calculation of moments. Dipole moments in the sense $^-Si=C^+$. Values in D)

	$H_2Si=CH_2$	$H_2Si=CF_2$	$F_2Si=CH_2$	$F_2Si=CF_2$
Charge densities				
Si—C σ bond	−0.726	−2.517	−0.087	−1.524
Si—C π bond	−2.017	1.596	−2.526	0.388
Si—X bond	0.431	0.142	3.095	2.747
C—Y bond	1.615	−0.829	1.766	−0.593
X lone pairs			−1.461	−1.405
Y lone pairs		1.274		1.178
sp atomic polarisations				
Si—C σ bond	−0.486	0.709	−0.572	0.197
Si—C π bond	0	0	0	0
Si—X bond	1.552	1.605	−0.108	−0.173
C—Y bond	−1.170	0.207	−1.120	0.177
X lone pairs			1.208	1.423
Y lone pairs		−1.702		−1.708
pd atomic polarisations				
Si—C σ bond	0.447	−0.182	0.272	−0.190
Si—C π bond	−1.988	−1.929	−1.969	−2.331
Si—X bond	0.843	0.601	0.222	−0.022
C—Y bond	−0.372	−0.025	−0.469	−0.072
X lone pairs			0.384	0.374
Y lone pairs		0.030		−0.014

TABLE 5

LOCALISED ORBITAL CONTRIBUTIONS TO DIPOLE MOMENTS OF GERMAETHYLENES $X_2Ge{=}CY_2$ (Burns orbitale. $sp'd''$ method for calculation of moments. Dipole moments in the sense $^{-}Ge{=}C^{+}$. Values in D)

	$H_2Ge{=}CH_2$	$H_2Ge{=}CF_2$	$F_2Ge{=}CH_2$	$F_2Ge{=}CF_2$
Charge densities				
Ge—C σ bond	0.175	−2.197	1.056	−1.569
Ge—C π bond	−0.701	3.062	−1.420	2.610
Ge—X bond	−0.248	−0.460	1.586	1.272
C—Y bond	1.029	−0.796	1.241	−0.625
X lone pairs			−0.855	−0.745
Y lone pairs		1.138		1.160
sp atomic polarisations				
Ge—C σ bond	−0.333	1.192	−0.794	0.796
Ge—C π bond	0	0	0	0
Ge—X bond	1.459	1.458	0.389	0.391
C—Y bond	−1.177	−0.109	−1.133	−0.141
X lone pairs			0.858	0.942
Y lone pairs		−1.276		−1.290
pd atomic polarisations				
Ge—C σ bond	0.260	−0.018	0.204	−0.045
Ge—C π bond	−0.1007	−0.704	−1.115	−0.960
Ge—X bond	0.399	0.260	0.060	−0.081
C—Y bond	−0.116	0.004	−0.169	−0.016
X lone pairs			0.143	0.112
Y lone pairs		0.034		0.029

due to the M—C π bonding orbitals. This then, is where the principal cause of the anomalous behaviour must lie.

In Fig. 1 are represented the variations of total dipole moment, the contribution due to the M—C π bonding orbital and the sum of the contributions from all the other localised orbitals for sila- and germa-ethylenes. In all cases the trend with substitution is seen to be in accordance with expectation for the sum of the non-π-bond contributions and in the opposite sense for the π bonds. However the amplitude of the variation in dipole moment occurring with these different components varies from system to system so that, while for the silaethylenes the effect of the π orbitals is more than cancelled out by the others, in the germaethylenes the effect due to the π bonds prevails when substitution at the carbon atom occurs, although the other bonds just manage to cause a slight shift in the expected direction when substitution occurs at the germanium atom.

It is not possible to ascribe the difference uniquely to either the π bonds or the remaining orbitals: the graphs for silaethylenes (with Burns orbitals) and germaethylenes are not obviously dissimilar, but the slight differences in relative amplitude are sufficient to give rise to the reversal of the trend with the germaethylenes. On the other hand, the π bond effect is present in all cases and is seen from the tabulated results to be associated chiefly with the charge density components. One is therefore brought to the conclusion that in such calculated molecular orbitals for sila- and germa-ethylenes, an anomalous distribution of charge in the M—C π bonding orbitals when fluorine is attached to the carbon atom occurs, causing not only withdrawal of electrons from the carbon but also an increase in

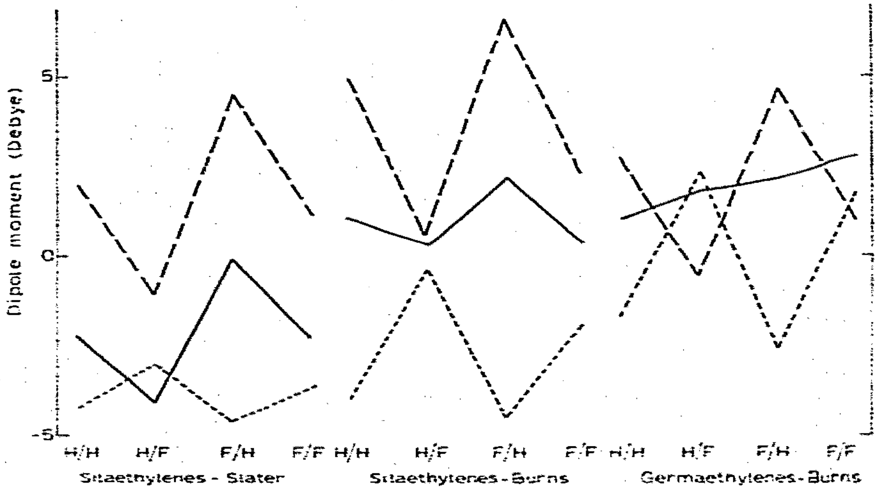

Fig. 1. Variation of dipole moment components of silaethylenes and germaethylenes with substitution. The symbol X/Y is used to represent $X_2M{=}CY_2$. Slater or Burns orbitals are used as indicated. Dotted line represents variation of M—C π bond dipole moment, dashed line the total of all other bond and lone pair dipole moments and solid line the total dipole moment for each molecule.

electron density at the other end of the π bond. The relative magnitude of this effect is so great in the case of the germaethylenes that it overcomes the other more obvious changes in the dipole moment and hence gives rise to the anomalous results.

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