Dipole Moment Derivatives and Infrared Intensities of SiH₄ and SiD₄

Kwan Kim¹ and Hwi Geon Lee

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151, Korea

(Received October 6, 1984)

The complete neglect of differential overlap (CNDO/2) approximate wavefunctions have been applied to select the preferred signs for the dipole moment derivatives of SiH₄ and SiD₄ in conjunction with the experimental alternatives. The apparent sign discrepancy from earlier reports has been identified. The effective atomic charge for hydrogen was found to be \( \chi_e = 0.229 \), more than two times larger in comparison with the values of typical hydrocarbons like CH₄. The anomalously large effective hydrogen charge was interpreted based on a quantum mechanical model as well as the value of atom anisotropy relative to effective atomic charge.

**Introduction**

Of the many pioneers in molecular spectroscopy, Mulliken was possibly the first to emphasize the importance of infrared intensities. He recognized that understanding this kind of data is essential for solving the central problem of chemistry; that is, for establishing the relationship between the properties of a material and its structure. However, during most of the period following Mulliken’s paper, only limited progress was made in interpreting infrared intensities. Based on his paper, it was taken as self-evident that an interpretive model of intensities must be founded upon the chemical bond concept. Recent efforts to resolve dipole moment derivatives into derivatives of chemical bond moment have resulted in sets of terms in which those describing the interactions between different bonds are of the same magnitudes as those defining the properties of a particular bond. Thus, unlike molecular energies, infrared intensities cannot be adequately reduced to a sum of terms that can be assigned to particular chemical bonds because of the importance of the interaction terms.

The problem of interpreting infrared intensities has improved dramatically within the last 10 years. That was because of the emergence of the concept of dipole moment derivatives as properties of the atoms in a molecule, rather than as properties of its chemical bonds. The atomic properties derived from intensities are, then, contained in the so-called atomic polar tensors and effective atomic charges. The atomic polar tensor for atom \( a \) in a molecule is defined as the conjugate (transposed) gradient of the molecular dipole moment vector, \( \mathbf{P} \), written in various notations as

\[
P_a = \nabla^* \mathbf{P} = \begin{bmatrix}
\partial P_x / \partial X_a & \partial P_y / \partial Y_a & \partial P_z / \partial Z_a \\
\partial P_x / \partial X_a & \partial P_y / \partial Y_a & \partial P_z / \partial Z_a \\
\partial P_x / \partial X_a & \partial P_y / \partial Y_a & \partial P_z / \partial Z_a
\end{bmatrix}
\]

and the square of the effective atomic charge is defined as one-third of the sum of squares of the polar tensor components, that is,

\[
\chi_a^2 = (1/3) \nabla^* \mathbf{P} \cdot \nabla \mathbf{P}.
\]

This development has led to the discovery of surprising order in intensity data. The polar tensors for a few, but ubiquitous atoms like hydrogen and fluorine, seem to be transferable properties that are characteristic of these atoms to a good approximation. Furthermore, the analysis of the integrated intensities of a variety of hydrocarbons, fluorocarbons, and other materials with diverse structures revealed that the effective charges for the hydrogen and fluorine atoms in these systems fell within fairly narrow range of values.

Above observations encourage further testing of the atomic
polar tensor and effective charges for various hydrogen compounds. In this paper we report the interpretation of the intensities of silane, which is the extension of our works on other systems like HCN\textsuperscript{4}, C\textsubscript{2}H\textsubscript{4}, SF\textsubscript{6}, CHF\textsubscript{3}, SO\textsubscript{2}Cl\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, SiF\textsubscript{4}, and C\textsubscript{4}H\textsubscript{2}N\textsubscript{2}. Previously Prasad et al.\textsuperscript{31} reported the effective hydrogen charge of SiH\textsubscript{4}. However, their criterion for choosing the preferred signs for the dipole derivatives with respect to normal coordinates that the correct signs correspond to values of the atomic effective charges which show a maximum difference for the central and terminal atoms was criticized not to be valid in general by many investigators\textsuperscript{16,25,33}. Furthermore, according to Prasad et al.,\textsuperscript{31} the effective hydrogen charge seems to be considerably larger in SiH\textsubscript{4} than those of usual hydrocarbons. Earlier, two exceptions were noted in the interpretation of intensities as atomic properties. The effective charges observed for the hydrogen atoms in C\textsubscript{2}H\textsubscript{4} and HCN were found to be about 2 times larger than the values common to the other carbon-hydrogen systems\textsuperscript{16,15}. In the previous report, however, those anomalously large effective charges could be adequately explained by virtue of their rather ionically bonded protons\textsuperscript{24}. We have, therefore, reinvestigated the polar tensor and effective charge of hydrogen atom in silane in order to determine definitely if the effective hydrogen charge in SiH\textsubscript{4} is really different from those of typical hydrocarbons like CH\textsubscript{4}.

**Method of Calculation**

The experimental value of the integrated intensity of the k-th fundamental mode of a molecule has been defined in two ways\textsuperscript{34,36},

\[ A_k = \left(1/\lambda l\right) \int \ln(L/\lambda) \, d\omega \]

or

\[ T_k = \left(1/\lambda l\right) \int \ln(L/\lambda) \, d\omega \]  

where, to a good approximation,

\[ A_k = \omega_0 I_k \]

In both, (\lambda l) denotes the product of the concentration of the absorbing species and sample thickness, \( L \) and \( \lambda \) are the incident and transmitted light intensity, respectively, and \( \omega_0 \) is the wave number at the band center. In the harmonic oscillator linear dipole approximation, the intensity is related to molecular structure in SI units by\textsuperscript{37}:

\[ A_k = \left(4 \pi \lambda I / 3 \, g_k \right) \left(\partial \hat{P}/\partial Q_k\right)^2 \]  

In this expression \( g_k \) denotes the degeneracy of the k-th mode, \( \partial \hat{P} / \partial K_k \) is the derivative of the dipole vector, \( \hat{P} \), with respect to the normal coordinate \( Q_k \), and the other symbols have their customary meaning.

To obtain structural information from intensities it is necessary to transform from normal coordinates to some other more interpretable coordinate set. Until recently, bond and valence angle coordinates, \( R = \{R_i\} \), were always chosen, and intensities were interpreted in terms of bond moments. Using the chain rule of differentiation, the transformations are readily carried out,

\[ \left(\partial \hat{P}/\partial Q\right) = \left(\partial \hat{P}/\partial R\right) \left(\partial R/\partial Q\right) \]

and

\[ \hat{P} = \left(\partial \hat{P}/\partial Q\right) \left(\partial Q/\partial R\right) \]

These are equivalent to expressions in the more customarily used matrix notation introduced by Person\textsuperscript{12} and Wilson\textsuperscript{37},

\[ \hat{P}_X = P_X L \quad \text{and} \quad \hat{P}_Z = P_Z L^{-1} \]

In (9), for example, \( (P_X)_{ij} = (\partial \hat{P}_i / \partial R_j) \) and \( (L)_{ij} = (\partial R_i / \partial Q_j) \).

In 1961, however, Biarge, Herranz and Morcillo\textsuperscript{4} broke with tradition and chose, instead, an atom-centered, Cartesian coordinate system, \( X \),

\[ \hat{P}_X = P_X L^{-1} B + P_x \beta \]

where \( B \) and \( \beta \) are the transformation matrices from the ordinary space fixed Cartesian coordinates to the internal coordinates and the \( \tau \) coordinates in equation (11), respectively. The explicit implication of \( P_x \) is given above in equation (1), and equation (12) is, therefore, the master equation used in this work such that the so-called polar tensor \( P_x \) would be obtained from the experimental data by transforming from \( P_x \) to \( P_z \).

We note that we may also transform from \( P_x \) to \( P_z \) by using the inverse relation of equation (10) to obtain,

\[ P_z = P_x A L, \]

where the matrix \( A \) is the inverse transformation from internal coordinates to Cartesian coordinates, defined so that \( BA = I \), a square identity matrix. Equation (13) has particular interest in that it is especially easy to calculate the polar tensor \( P_x \) from quantum mechanical procedures. One simply calculates the dipole moment at equilibrium and again after a small displacement in the well defined space-fixed \( X \) direction of the \( \sigma \) atom. The difference in the \( X \) component divided by the displacement is taken to be the approximately the derivative,

\[ \partial P_x / \partial X_\sigma \Delta X_\sigma \]

The change in the total dipole moment vector when the \( \sigma \) atom is displaced in the \( X \) direction also gives \( \partial P_x / \partial X_\sigma \) and \( \partial P_x / \partial X_\sigma \). Similarly we can evaluate the other terms in the polar

![Figure 1](image-url)  

**Figure 1.** Coordinate axes and molecular orientation of silane used in normal coordinate calculation.
TABLE 1: Structural Data and Definition of Internal and Symmetry
Coordinates of Silane

| Masses (u) | m_b = 27.976928 m_h = 1.007825 m_o = 2.014102 |
| Structure | R_m = 0.1481 nm |
| Internal coordinates: | \[ R_i = d_{o1i} \] |
| | \[ R_i = d_{o3i} \] |
| | \[ R_i = d_{o4i} \] |
| | \[ R_i = d_{o5i} \] |
| | \[ R_i = d_{o6i} \] |

Symmetry coordinates:

<table>
<thead>
<tr>
<th>C_n</th>
<th>T_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_i</td>
<td>[ S_i = (1/2) (R_i + R_j + R_k) ]</td>
</tr>
<tr>
<td>A_i</td>
<td>[ F_i = (1/\sqrt{2}) ] (R_i - R_j - R_k)</td>
</tr>
<tr>
<td>A_i</td>
<td>[ E_i = (1/\sqrt{2}) ] (R_i + R_j + R_k)</td>
</tr>
<tr>
<td>A_i</td>
<td>[ E_i = (1/\sqrt{2}) ] (R_i - R_j - R_k)</td>
</tr>
<tr>
<td>A_i</td>
<td>[ A_i = (1/\sqrt{2}) (R_i + R_j + R_k) ]</td>
</tr>
</tbody>
</table>

*Ref. (38); *Ref. (39)*: The subscripts refer to the atoms shown in Figure 1; \( r_o \) is a Si-H bond and \( a_{oH} \) is a H3SiH angle.

\[ \text{tensor } P_{ij}, \text{ and combine them to obtain } P_{ij}. \text{ Using equation (13), we can then convert the calculated polar tensor to } P_{ij}, \text{ which can be compared with the experimental value.} \]

The polar tensor values of silane were calculated by means of equation (12) using \( \rho_H \) values of Ball et al.\(^{30}\). The rotational and translational contribution to \( P_{ij} \), \( P_{ij} \), is zero because of the null equilibrium dipole moment and charge. The Cartesian coordinate axes, numbering of atoms, and orientation of silane molecule are shown in Figure 1. The equilibrium structural data, and the definition of the internal and symmetry coordinates are listed in Table 1. The \( L \) matrices were calculated using the harmonic force field reported by Duncan\(^{38}\). These values are given in Table 2. The B matrix was evaluated using Wilson's method\(^{39}\).

Results and Discussion

\( G \) sum rule graphs employing abscissas and ordinates expressed in terms of squares of atomic effective charges are very useful in comparing the accuracies of infrared fundamental sum values for isotopically related molecules. The \( G \) sum rule for silane and its deuterated analogues is given by\(^{37}\)

\[ \frac{1}{K} \sum L_i \frac{\rho_i^2}{m_i} \frac{m_i}{m_n} \left( n_a - n_b \right) \frac{1}{m_n} \]

where \( K = N_a^2/e_0 c^2 \) and \( L_i \) is the fundamental intensity sum. \( \rho_i^2 \) and \( m_i \) are atomic effective charges and masses and \( m_n \) is equal to the number of hydrogens in the molecule under study. In Figure 2, graphical representations of the \( G \) sum rule for the intensity data of SiH\(_4\), SiHD\(_4\), and SiD\(_4\) are presented. Since the \( v_2 \) band intensity of SiHD\(_3\) was not reported in Ball's paper, it has been assumed here that his value is about 30% greater than that of Levin et al.\(^{37}\), for Ball's intensity data are 30% greater at a moderate estimate than those of Levin et al. for other bands in SiHD\(_3\). The figure clearly shows that although the SiH\(_4\), SiD\(_4\), and SiHD\(_4\) data of Ball et al. result in an intersection yielding positive values for \( \chi^H \) and the isotopically invariant quantities, \( \chi^D \) and \( \chi^H \), the intersection of the \( G \) sum rule lines for the data of Levin et al. implies imaginary values for the effective charge of silicon atom. One must conclude that the intensity sums for the data of Levin et al. are less accurate and somewhat inconsistent with the sums for the data of Ball et al. In this respect we have employed Ball's intensity data for the subsequent analysis.

Prasad et al.\(^{49}\) reported the preferred sign of dipole moment derivatives with respect to normal coordinates, \( \partial P/\partial Q \), and \( \partial P/\partial Q \), for SiH\(_4\). However, as mentioned above recalculation is necessary in order to ensure that the sign conventions are consistent throughout the treatment. In Table 3 representative values for silicon atom, hydrogen atom 1, and hydrogen atom 2 of Figure 1 for the atomic polar tensors of SiH\(_4\) and SiD\(_4\) are given. The experimental errors for the individual polar tensor elements are given in parenthesis. The best agreement for the expected isotopically invariant elements of these ten-
sors occurs for the (±) sets for SiH₄ and the (±) sets for SiD₄.
The differences between the respective polar tensor elements of these sets are either smaller than the sum of the experimental errors of these elements for SiH₄ and SiD₄ or they are slightly larger. The error estimates reported here are minimum values as they contain no contributions due to errors in the normal coordinates. Consideration of these errors could easily increase our error estimates for each of the polar tensor elements by 0.002 e which is sufficient to obtain agreement between all the individual elements of these sets.

In order to reach some decision about which of the several possible polar tensors are correct for silane, we may compare the different possible sets of the P values from the experimental data with the calculated values from the CNDO/2 quantum mechanical calculations, which are given in Table 4. Comparison of the calculated results with the possible experimental results leads us to prefer one sign combination. The calculated values of \( \Delta \beta \) agree reasonably well in magnitude and sign with the experimental dipole moment derivatives from the (±) sign combinations (\( \Delta \beta \)) for both of SiH₄ and SiD₄. It is generally difficult however to predict quantitatively the dipole moment derivatives from approximate quantum mechanical treatments. Nevertheless, the \( \Delta \beta \) values are large enough to leave no room for doubt about the proper sign choice. In particular any doubts remaining about

---

**Figure 2.** G-sum rule graphs for SiH₄, SiD₄, and SiHD₃. -- Ball et al’s data in ref. (28); ---, Levin et al’s data in ref. 1311.

**Table 3: Atomic Polar Tensors of Silane Given in Multiples of e**

<table>
<thead>
<tr>
<th></th>
<th>P^±×10^3</th>
<th>P^±±×10^3</th>
<th>P^±±++×10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>P^±</td>
<td>±0.207 0 0</td>
<td>±0.207 0 0</td>
<td>±0.207 0 0</td>
</tr>
<tr>
<td>SiH₄</td>
<td>0 0</td>
<td>0 0</td>
<td>0 0</td>
</tr>
<tr>
<td>P^±±</td>
<td>±0.227 0 0</td>
<td>±0.227 0 0</td>
<td>±0.227 0 0</td>
</tr>
<tr>
<td>SiD₄</td>
<td>0 0</td>
<td>0 0</td>
<td>0 0</td>
</tr>
<tr>
<td>P^±±±</td>
<td>±0.227 0 0</td>
<td>±0.227 0 0</td>
<td>±0.227 0 0</td>
</tr>
<tr>
<td>SiH₄</td>
<td>0 0</td>
<td>0 0</td>
<td>0 0</td>
</tr>
</tbody>
</table>

*Intensities of silane in ref. (28) were used in this calculation; *The signs are the signs of the \( \Delta P/\Delta Q \) for each element of the tensor. For example, (±) would mean that the signs of \( \Delta P/\Delta Q \), and \( \Delta P/\Delta Q' \), are both either positive or negative; *The atomic polar tensor of hydrogen atom number 2 in Figure 1. *The value with upper sign (±) is obtained from the signs of \( \Delta P/\Delta Q \) corresponding to the upper sign combination (+) in two sets of sign choices (±). See note b above; *The values in parenthesis represent the uncertainties based on the estimated errors in the reported intensities; *These tensors were calculated using the CNINDO program 141 from QCPE.
the certainty of the (−+) sign choice may be dispelled by careful examination of Table 3, comparing the atomic polar tensors calculated by the quantum mechanical method with those obtained from the experimental data. Although there may still be some doubt on the possibility of signs of $\delta P/\delta Q$ and $\delta P/\delta Q_{i}$ being both positive, this sign choice gives the polar tensors not only considerably small in magnitude for silicon atom but also exact opposite in sign for the $P_{o}$ element of $P^{(2)}$. It is therefore quite clear that the values calculated agree with the (−+) sign choice and do not agree with the values derived from other sign choices. Thus we believe that the examination of intensity data in the form of atomic polar tensors may be useful in trying to decide such delicate matters as the sign choice to be preferred.

As described above prasad et al.24 suggested that one criterion for choosing the preferred signs for the $\delta P/\delta Q_{i}$'s be that the signs should be preferred that resulted in a maximum value for the difference between the square of the effective charge $\chi_{\alpha}^{2}$ on the central atom (here silicon) and the sum of $\chi_{\alpha}^{2}$ values for the terminal atoms (here hydrogen). The preferred sign choices for SiH₄ and SiD₄ give $\chi_{\alpha}^{2}$ values for the terminal atoms (here hydrogen)4. The preferred sign choices for SiH₄ and SiD₄ give $\chi_{\alpha}^{2}$ values for the central atom (here silicon) and the sum of $\chi_{\alpha}^{2}$ values for the terminal atoms (here hydrogen)4. The preferred sign choices for SiH₄ and SiD₄ give $\chi_{\alpha}^{2}$ values for the terminal atoms (here hydrogen)4. The preferred sign choices for SiH₄ and SiD₄ give $\chi_{\alpha}^{2}$ values for the terminal atoms (here hydrogen)4. The preferred sign choices for SiH₄ and SiD₄ give $\chi_{\alpha}^{2}$ values. However, since we do not believe there is any physical reason to prefer a maximum or minimum value for this function, we suggest that this criterion be abandoned. Incidentally, it is of some interest to note that prasad et al.24 obtained the different sign choice (−−) using their criterion although their values of effective charges were almost the same as we got. However, one must realize that the signs of $\delta P/\delta Q_{i}$ values are meaningless without the detailed knowledge of all the definitions used to obtain them. Comparing prasad et al.'s values of $\chi_{\alpha}$ with ours shows that their (−−) convention for the signs of $\delta P/\delta Q_{i}$'s corresponds to our (−+) convention. We believe there was an inconsistency in the definitions of their normal coordinate calculation.

The results reported here provides additional information on the nature of hydrogen atom effective charges. Since both elements of carbon and silicon belong to group IV in periodic table, it may be interesting to compare the effective hydrogen charge of silane with those of various hydrocarbons. Table 5 contains the effective charges of hydrogen atom for various compounds. This table reveals rather surprising feature that the effective hydrogen charges fall within the ranges in all of the systems listed in Table 5. These results suggest that the effective charge represents a particularly localized combination of chemical bond properties of, whose magnitude is most sensitive to the nature of the particular atom and much less sensitive to the nature of other atoms in its vicinity or their geometrical arrangement. It is curious, however, that the effective hydrogen charge in silane shows significant difference from the "typical" value of about 0.1 $e$ for all compounds in Table 5 except CH₂ and HCN. The anomalously large effective hydrogen charges in CH₂, HCN, and SiH₄ must be rationalized. Just as there is no obvious reason that the effective hydrogen charge in some compounds should be equal, there is no obvious reason that the effective charge for other compounds should deviate so sharply from the others. Indeed, it may not be clear which are the anomalous systems. Whichever point of view is chosen, one cannot resist pointing out one major difference between the properties of hydrogen atoms considered in Table 5. On the basis of author's recent finding46 that the value of the atom anisotropy relative to the effective atomic charge is a very useful parameter in characterizing chemical bonds in terms of atomic properties, CH₂, HCN and SiH₄ fall into one group and other compounds in Table 5 fall into another group. The atom anisotropy, $\beta^{\alpha}$, has been defined as43

$$\chi_{\alpha} = (P_{o})' + (2/3) \beta^{\alpha}$$

where $\chi_{\alpha}$ is the effective charge of atom $\alpha$ in a molecule and $P_{o}$ is the so-called mean dipole derivative defined as43

$$\overline{P_{o}} = \frac{1}{3} \mathbf{T}_{\alpha} \mathbf{P}_{\alpha}$$

that is, one third of the trace of atomic polar tensor of atom $\alpha$. The values of author's new parameter $a_{\alpha}$ ($V_{d}^{\alpha} / 3\chi_{\alpha}$) for CH₂, HCN and SiH₄ are close to 0, the value for a fixed charge. On the other hand, the values of $a_{\alpha}$ for other molecules in Table 5 are rather close to 1. The differences in the values of $a_{\alpha}$ between these two groups of molecules may indicate the different extent of the mobility of the hydrogen atoms in the molecular systems considered here. According to the argument given in the previous report46 for the cases of HCN and CH₂, the anomalously large effective hydrogen charge in SiH₄ may be ascribed to the largely ionic character of its bonded protons.
in comparison with typical hydrocarbons like CH₄. Indeed, semi-empirical CNDO/2 calculation has shown in this work that Mulliken’s net hydrogen charge ₂₀, ₂₁ in SiH₄ is more than 10 times greater compared with that of CH₄. These observations would, perhaps, be indicative of the fact that the problem of interpreting infrared intensities can be treated in a more simple and precise way by using the so-called “atomic effective charge”.

To further understanding of the anomalously large hydrogen atom effective charge in silane compared with those of hydrocarbons, it will be useful to consider a quantum mechanical model for the polar tensor. Formal expressions for the polar tensor are readily obtained by computing the gradient of the dipole moment. The dipole moment is a measure of the vector difference between the centroids of positive and negative charges in a molecule. For example, in the Born–Oppenheimer approximation this difference is defined, in natural unit ₂², as

$$ P(R) = \sum_{n} q_{n} \hat{r}_{n} - \int \rho(\hat{r}; R) d^{3} \hat{r} $$

in which \( \hat{R} \) denotes the set of nuclear position vectors, \( \hat{r}_{n} \), \( q_{n} \) the atomic number of nucleus \( n \), and

$$ \rho(\hat{r}; R) = \int |\psi(\hat{r}, \hat{r}_{1}, ..., \hat{r}_{n})|^{2} d^{3} \hat{r}_{1} ... d^{3} \hat{r}_{n} $$

the electron number density at point \( \hat{r} \) in an \( N \)-electron molecule. Any model dependence in a calculation of polar tensor is introduced by way of the representation chosen for the number density function, \( \rho(\hat{r}; R) \) or equivalently, the molecular wave function, \( \psi(\hat{r}; R) \), in (19). Since polar tensors are expressed in terms of the Cartesian coordinates of the atoms in a molecule, \( \rho(\hat{r}; R) \) is most conveniently represented as a multi-centered expansion in complete sets of orthonormal atomic orbitals centered on each nucleus; that is,¹⁴

$$ \rho(\hat{r}; R) = \sum_{\alpha} \Sigma_{\hat{r}_{\alpha}} C_{\alpha}^{\hat{r}_{\alpha}} \phi_{\alpha}^{*}(\hat{r}_{\alpha}) \phi_{\alpha}(\hat{r}_{\alpha}) $$

in which, for example, \( \hat{r}_{\alpha} = (\hat{r} - \hat{R}_{\alpha}) \), \( \phi_{\alpha}(\hat{r}_{\alpha}) \) denotes the i-th orbital centered on nucleus \( \alpha \), and \( C_{\alpha}^{\hat{r}_{\alpha}} \) is the the one-electron density matrix element. To further partition (20) into independent atomic contributions, the cross-terms are eliminated by expanding the orbitals centered on one nucleus in terms of orbitals centered on another,

$$ \phi_{i}(\hat{r}_{\alpha}) = \sum_{\alpha} S_{\alpha i}^{\ast}(\hat{R}_{\alpha}) \phi_{\alpha}^{*}(\hat{r}_{\alpha}) $$

where \( \hat{R}_{\alpha} = |\hat{r} - \hat{R}_{\alpha}| \) is the internuclear distance and \( S_{\alpha i} = \langle \phi_{i}(\hat{r}_{\alpha}) | \phi_{\alpha}(\hat{r}_{\alpha}) \rangle \) is the overlap integral. Substitution of (21) into (20),

$$ \rho(\hat{r}; R) = \sum_{\alpha} \sum_{\beta} N_{\alpha \beta}^{\ast} \phi_{\alpha}^{*}(\hat{r}) \phi_{\beta}(\hat{r}) $$

where

$$ N_{\alpha \beta} = \sum_{\alpha} \Sigma_{\hat{r}_{\alpha}} C_{\alpha}^{\hat{r}_{\alpha}} S_{\alpha i}^{\ast}(\hat{R}_{\alpha}) $$

Integration of (22) over the position variables for an \( N \) electron system yields

$$ N = \int \rho(\hat{r}; R) d^{3} \hat{r} = \sum_{\alpha} N_{\alpha}(\hat{R}) $$

where

$$ N_{\alpha}(\hat{R}) = \sum_{\beta} N_{\alpha \beta}^{\ast}(\hat{R}) $$

is the gross population density defined by Mulliken ₂₂ . Substituting (22) into (18), and making use of the relation \( \hat{f} = \hat{f}_{p} + \hat{f}_{a} \), yields the molecular dipole moment as a sum over atomic terms,

$$ P(R) = \sum_{\alpha} \sum_{\beta} N_{\alpha \beta}^{\ast}(\hat{R}) - \sum_{\alpha} \phi_{\alpha}(\hat{r}) $$

where

$$ \zeta_{\alpha}(\hat{R}) = q_{\alpha} - N_{\alpha}(\hat{R}) $$

is Mulliken’s net atomic charge, and

$$ \phi_{\alpha}(\hat{r}) = \sum_{\beta} N_{\alpha \beta}^{\ast}(\hat{R}) $$

Differentiation of (24) finally yields the polar tensor,

$$ \nabla_{\alpha} \cdot P = \zeta_{\alpha} + \sum_{\beta} \nabla_{\alpha} \cdot \phi_{\alpha}^{*}(\hat{r}) $$

Several models for interpreting infrared intensities can be identified with the terms in eq. (27). The first two terms, in particular, describe the polar tensor obtained in a classical atomic charge model ²⁶ . The first term describes the contribution of a “net atomic–charge” which follows the motion of the nucleus perfectly, and the second term describes the “charge flux” resulting from the transfer of charge from one nucleus to another as the result of nuclear displacement. The third term is strictly a quantum mechanical term which has no classical analogue. This term arises solely from interference phenomena resulting from the superposition of wave functions. Unfortunately, there is no experimental way of resolving polar tensors into these terms, and they must be estimated by calculation.

The results of such calculations for two representative systems, CH₄ and SiH₄, are summarized in Table 6. There, theoretically estimated polar tensors for the hydrogen atoms in CH₄ and SiH₄, obtained by CNDO/2 calculations, are compared with those obtained from experimental intensities. In both calculations the CH and SiH bonds are coincident with the Z coordinate axis. For axes oriented in this way, the polar tensors are diagonal by symmetry, so that the diagonal elements are listed.

**TABLE 6: Comparison to Hydrogen Polar Tensors in SiH₄ and CH₄ Obtained by CNDO/2 Calculations and by Experiments, in Natural Units(e)**

<table>
<thead>
<tr>
<th></th>
<th>XX(=YY)</th>
<th>ZZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \zeta_{\alpha}^{f} )</td>
<td>0.012</td>
<td>0.012</td>
</tr>
<tr>
<td>( \Sigma_{\alpha \beta}^{\ast} \hat{R}_{\alpha} )</td>
<td>0.046</td>
<td>0.093</td>
</tr>
<tr>
<td>( -\Sigma_{\alpha \beta}^{\ast} \phi_{\alpha} )</td>
<td>-0.015</td>
<td>-0.218</td>
</tr>
<tr>
<td>( \nabla_{\alpha} \cdot P ) (calc)</td>
<td>0.043</td>
<td>-0.113</td>
</tr>
<tr>
<td>( \nabla_{\alpha} \cdot P ) (obs)</td>
<td>0.064</td>
<td>-0.139</td>
</tr>
<tr>
<td>( x_{\alpha} ) (calc)</td>
<td>0.074</td>
<td>0.096</td>
</tr>
<tr>
<td>( x_{\alpha} ) (obs)</td>
<td>0.289</td>
<td>0.029</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SiH₄</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \zeta_{\alpha}^{f} )</td>
<td>-0.150</td>
<td>-0.150</td>
</tr>
<tr>
<td>( \Sigma_{\alpha \beta}^{\ast} \hat{R}_{\alpha} )</td>
<td>0.036</td>
<td>0.037</td>
</tr>
<tr>
<td>( -\Sigma_{\alpha \beta}^{\ast} \phi_{\alpha} )</td>
<td>-0.197</td>
<td>-0.146</td>
</tr>
<tr>
<td>( \nabla_{\alpha} \cdot P ) (calc)</td>
<td>-0.311</td>
<td>-0.261</td>
</tr>
<tr>
<td>( \nabla_{\alpha} \cdot P ) (obs)</td>
<td>-0.227</td>
<td>-0.232</td>
</tr>
<tr>
<td>( x_{\alpha} ) (calc)</td>
<td>0.235</td>
<td>0.029</td>
</tr>
<tr>
<td>( x_{\alpha} ) (obs)</td>
<td>0.229</td>
<td>0.029</td>
</tr>
</tbody>
</table>

*Ref (10); *Average of values derived from data in ref. (28). See Table 3.
Possibly the safest general conclusion to be drawn from these calculations is that all three of the constituent parts of the polar tensors, defined in eq. (27), are significant. Thus, none of the three groups of terms in eq. (27) can be completely neglected in these systems and presumably in others as well. In the two systems considered in Table 6, the "interference" term, \( \frac{-2}{3} \sin \theta_{tt} \), is a dominant one, but the other terms make comparable contributions. The "perfect following" term reflects, in part, the difference in the electronegativity between central (C or Si) and terminal (H) atoms. The excessively large value of this term in SiH\(_4\) compared with that in CH\(_4\), is consistent with the foregoing that SiH\(_4\) is more ionic than typical hydrocarbons like CH\(_4\). Coupled with this first term, the fairly large \( XX(=YY) \) component of the "interference" term in SiH\(_4\) seems to render the effective hydrogen charge of this molecule to be anomalously large. In addition, one may note that, in SiH\(_4\), the \( XX(=YY) \) and \( ZZ \) components are nearly the same not only in magnitude but also in sign for the three groups of terms in eq. (27). These facts are, thus, the finding that the value of the hydrogen anisotropy relative to the effective hydrogen charge in SiH\(_4\) is close to 0, contrary to the cases of typical hydrocarbons like CH\(_4\), whose values are rather close to 1. The \( XX \) component of the "interference term" may reflect specifically the more labile character of electrons in SiH\(_4\) as compared with CH\(_4\). Thus, as we suggested in previous report\(^4\), the magnitude of the anisotropy relative to the effective atomic charge would potentially be a very useful parameter in characterizing chemical bonds in terms of atomic properties only from the infrared intensity data.

In conclusion we see that G sum rule is very useful in comparing the accuracies of infrared fundamental sum values for isotopically related molecules, and that it is very easy to have apparent inconsistencies in signs due to inconsistencies in the arbitrary sign conventions occurring in the calculation of dipole moment derivatives, unless one person carries through the entire calculation from start to finish. When the sign conventions are consistent, the values of \( \delta P/\delta S \) or of polar tensor elements calculated by the quantum mechanical method are in surprisingly good agreement with experiment. The best values for the H- and Si-atom polar tensors in silane are believed to be given in the (−) column of Table 3. The effective hydrogen charge was found to be \( \psi = 0.229 \pm 0.002 \), somewhat larger value compared with those of usual hydrocarbons. The effective hydrogen charge in silane was ascribed to the largely ionic character of its bonded protons in comparison with typical hydrocarbons like CH\(_4\). According to the quantum mechanical model, it was found that the "interference term" is excessively large in the polar tensors, leading to the more labile character of electrons in silane. Combined with above observations, it is likely that the value of the atom anisotropy relative to the effective atomic charge would potentially be a very useful parameter in understanding the chemical bonds solely from the vibrational intensity measurement.

Acknowledgement. This work was supported by Ministry of Education in Korea.

References

6. This definition differs from the original one, Ref. 5, by the factor 1/3.
A Wittig Route to (Z)-13-Eicosen-10-one, the Pheromone of the Peach Fruit Moth, and Its Biological Activity Test

Suk-Ku Kang† Jung-Min Park and Kyung-Ok Yoo

Department of Chemistry, Sung Kyun Kwan University, Natural Sciences Campus, Suwon 170, Korea

Jeong-Oon Lee and Hyun-Gwan Goh

Department of Entomology, Institute of Agricultural Science, O.R.D., Suwon 170, Korea

(Received October 24, 1984)

(Z)-13-Eicosen-10-one, an active component of the sex pheromone of the peach fruit moth was synthesized from 4-oxo-tridecan-1-carboxylic acid and heptylidene-triphenylphosphonium ylide by Wittig reaction. The key intermediate, 4-oxo-tridecan-1-carboxylate was synthesized by three different methods. The biological activity test of the synthetic pheromone as an attractant for the male peach fruit moth was tested at several districts in Korea.

Introduction

(Z)-13-Eicosen-10-one, an active component of sex pheromone of the peach fruit moth, Carposina nipponensis Walshingham, a major economic pest of apple, peach and other fruits was isolated by Tamaki in 1977. Structurally, while most lepidopterous pheromones were characterized as unsaturated alcohols, acetates, or aldehydes of 12-, 14-, 16-, or 18-carbon chain length, the sex pheromone of the peach fruit moth is an exceptional unsaturated aliphatic ketone. Several syntheses of (Z)-13-eicosen-10-one have been reported. In 1982, Yoshida reported the synthesis of (Z)-13-eicosen-10-one via salt-free Wittig reaction of heptylidene-triphenylphosphonium ylide and 4-oxo-tridecan-1-carboxylic acid. 4-Oxo-tridecan-1-carboxylate was prepared from 1-[(p-tolylsulfonyl) nornone and methyl 4,4-dimethoxybutanoate. Recently, 4-oxo-tridecan-1-carboxylate was synthesized by Hernandez by addition of n-nonyllithium to y-butyrolactone followed by PCC oxidation of the resulting alcohol in his synthesis of (Z)-13-eicosen-10-one. In 1981, Naoshima reported a synthesis of (Z)-13-eicosen-10-one via the Wittig olefination of 4-oxo-tridecan-1-carboxylate with heptylidene-triphenylphosphonium ylide in toluene in the presence of 12-crown-4-ether. In this report, 4-oxo-tridecan-1-carboxylate was prepared from diethyl 2-oxo-glutarate in five steps.

Institute of Agricultural Sciences in Suwon, Korea needed a fair amount of the pheromone of the peach fruit moth to conduct field test experiments in Korea. We therefore undertook to develop some practical methods for the synthesis of the pheromone of the peach fruit moth.

We wish to report a practical synthesis of (Z)-13-eicosen-10-one via the Wittig olefination of 4-oxo-tridecan-1-carboxylate with heptylidene-triphenylphosphonium ylide. The key intermediate, 4-oxo-tridecan-1-carboxylate was prepared by three different synthetic methods. Also we wish to report the results of the biological activity test as an attractant for males of the peach fruit moth.

Results and Discussion

It has been well established that the Wittig reaction when carried out between aliphatic aldehyde and aliphatic non-stabilized triphenylphosphonium ylide in salt-free, nonpolar solvent or in polar aprotic solvents such as DMF, DMSO or HMPA gives Z-alkenes stereoselectively. It has been known that only aldehyde reacts with phosphonium ylide in the presence of ketone. A simple retrosynthetic analysis (Scheme 1) reveals that 4-oxo-tridecan-1-carboxylate is the key intermediate.

We have prepared 4-oxo-tridecan-1-carboxylate, the key intermediate by three different methods and synthesized the pheromone of the peach fruit moth by olefination reaction of 4-oxo-tridecan-1-carboxylate.

(1) Grignard Route. 4-Oxo-tridecan-1-carboxylate was prepared from commercially available acrolein and decanoyl chloride (Scheme 2).

1,4-Addition of HBr to acrolein, followed by protection of the aldehyde portion with 1,3-propanediol afforded 2-(2-bromoethoxy)-1,3-dioxane. Grignard reagent from 2-(2-bromoethoxy)-1,3-dioxane and Mg in THF was added to