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A COMPARISON OF THE ROLE OF CHARGE TRANSFER, HYPERCONJUGATION, INDUCTIVE AND FIELD INTERACTIONS IN SUBSTITUTED METHYL AND SILYL SUBSTITUENT EFFECTS ON BENZENE π VERTICAL IONIZATION ENERGIES

BRIAN G. RAMSEY

Department of Chemistry, University of Oregon, Eugene, Oregon (U.S.A.) and Institute for Inorganic Chemistry, University of Frankfurt, Frankfurt/Main (Germany)

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Summary

The first two vertical π-ionization energies of MX_3 substituted benzenes as determined by photoelectron spectroscopy are compared with the results of modified CNDO/2 calculations, where M is Si or C and X is H, F, Cl and OCH_3. The major substituent interaction mechanisms of MX_3 are described within the CNDO/2 model. The results for methylorthobenzoate support intramolecular charge transfer stabilization of the benzene radical cation ground state by oxygen lone pair electrons, whereas the dominant interaction of the $Si(OCH_3)_3$ group is a positive charge stabilising field effect. The first vertical ionization energies of $PhSiCl_3$ and $PhCCl_3$ are unexpectedly assigned to ionization from the a' π orbital rather than the a'' orbital nodal at the substituent site. Carbon—chlorine hyperconjugation is a suggested stabilizing interaction in the $PhCCl_3$ $^2A'$ cation. The shape of the first band in the PE spectrum of phenylsilane is described as a possible example of a pseudo Jahn—Teller effect. Unlike CX_3, SiX_3 substituents except, where X is methoxy, exhibit calculated opposing field and σ-inductive effects.

The ionization process in photoelectron spectroscopy (PES) may be correctly considered from the viewpoint of a gas-phase chemical reaction in which a measured vertical ionization energy represents the difference in energy between reactant and product in their appropriate electronic states but with the same nuclear geometry. Viewed then as a chemical reaction, it is appropriate to examine substituent effects on the π-ionization energies of benzene to see to what extent and how the traditional substituent interaction models of organic chemistry apply to this process in determining changes in ionization energy.

In this work, attention is focused on differences in substituent interaction mechanisms as described by semiempirical modified CNDO/2 calculation which correlate the lowest two vertical π-ionization energies of substituted silyl- and substituted methyl-benzene, $C_6H_5MX_3$, with the negative value of the molecular orbital energies.

The results serve to illuminate some important differences between the interactions of CX_3 and SiX_3 substituents with π systems.

Results and discussion

The first two vertical π-ionization energies I^v, determined by PES of $C_6H_5MX_3$ (M is C or Si, X is H, Cl, F, OCH_3), and other relevant molecules are collected in Table 1 along with the energies of the highest two π-molecular orbitals as calculated by a modified CNDO/2 procedure. Because in general the bands are broad and featureless, an error of ±0.03 eV is estimated in I^v.

The CNDO/2 program has been extensively used and it is described in detail elsewhere [1]. The modifications are essentially those of Jaffe and Del Bene [2] in which CNDO/2 parameters are chosen to fit electronic transitions. Calculations for SiX_3 derivatives were carried out both with (CNDO/2) and without (CNDO/2′) Si *d*-orbitals in the basis set, even though it is known that this program overestimates to some extent the importance of the *d* functions [3].

For symmetry assignments, the substituted benzenes have, as a single symmetry element, a y, z plane perpendicular to the benzene ring and passing through C(4), C(1), M and one X. The first two π-ionization energies are designated a' or a'' according to whether the originating π-molecular orbital is symmetric or antisymmetric with respect to the y, z plane, II (a', a'').

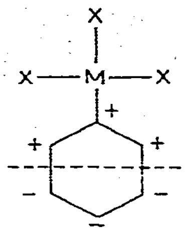
The local geometry chosen for $M(OCH_3)_3$ substituents was one which pro-

TABLE 1

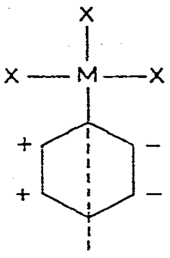
FIRST TWO OBSERVED IONIZATION ENERGIES OF SUBSTITUTED BENZENE AND CALCULATED EIGENVALUES (eV)

Substituent	$I^V(\pi)$	$I^V(\pi)$	$-\epsilon^{CNDO}_{(a')}$	$-\epsilon^{CNDO}_{(a'')}$
CH_3	8.89 [a]	9.32 [a]	10.26	10.62
SiH_3	9.25	9.53	10.86	10.74
SiH_3 [b]	9.25	9.53	10.42	10.56
CCl_3	9.32	9.6 [d]	10.78	11.08
$SiCl_3$	9.46	9.7 [d]	11.29	11.14
$SiCl_3$ [b]	9.46	9.7 [d]	11.17	11.15
$SnCl_3$	9.78	10.0	—	—
CF_3	9.75	10.1 [d]	11.23	11.19
SiF_3	9.83	10.1 [d]	11.67	11.34
SiF_3 [b]	9.83	10.1	11.46	11.28
$C(OCH_3)_3$	9.03	9.38	10.38	10.62
$Si(OCH_3)_3$	8.96	<9.2 [e]	10.36	10.39
$Si(OCH_3)_3$ [b]	8.96	<9.2 [e]	10.56	10.60
p-CH_3O, $SiCl_3$	8.75	9.61	—	—
p-CH_3O, $Si(OCH_3)_3$	8.34	9.17	—	—
CH_3O	8.42	9.28	—	—
H	(9.32) [c]	(9.32) [c]	10.64	10.64

[a] Band center, see text. [b] CNDO/2′, *d* orbitals omitted. [c] Jahn—Teller corrected from 9.25 and 9.53 eV first and second I^V. Error is regarded within +0.05 eV. See Text. [d] Shoulder. [e] No shoulder resolved, band broadened to high energy side.

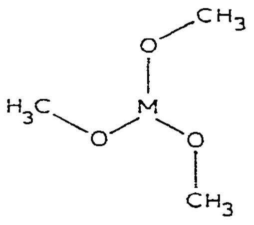


(II) (a′)



(II) (a″)

vided minimum steric hindrance for the methyl groups and at the same time maximum oxygen p_y overlap with the benzene π system. Local symmetry at the $M(OCH_3)_3$ group is, therefore, C_3 (III), rather than C_{3v} (IV).



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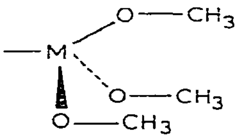


(IV)

The I^v of a PES band split by vibrational components should be correctly taken as the intensity weighted average, or centroid, of the vibronic ionization energies, For this reason the I^v of toluene is considered to be closer to 8.89 eV than the most intense vibrational component at 8.82 eV. In most of the spectra considered here, however, the vibrational components were not resolved and I^v was estimated in the usual way as the band maximum.

In Jahn—Teller split PES maxima of doubly degenerate cation states, as is the case for the first PES band of benzene, the I^v lies between the minimum of the Jahn—Teller envelope and the most intense PES maximum [4]. The vertical ionization energy of benzene as it relates to the degenerate pair of benzene π orbitals must be greater than the 9.25 eV observed for the first intense adiabatic ionization energy. A somewhat arbitrary correction of 0.07 eV, which is one quarter of the difference between the benzene PES maxima at 9.25 and 9.53 eV, is taken as a conservative lower estimate for the benzene I^v, 9.32 eV. The a'' π I^v of *p*-xylene was measured at 9.19 eV. If methyl substituent effects on the a'' π I^v are additive, a benzene I^v of 9.45 eV is estimated from the removal of one methyl from toluene. Konig [7] has estimated a value of about 9.35 eV from the I^v of toluene, *p*-xylene, and mesitylene. A least square correlation of $C_6H_5CX_3$ I^v known within ±0.03 eV with CNDO/2 $\epsilon(a', a'')$ predicts a benzene I^v of 9.32 eV.

It has been a wide spread and mistaken practice in past interpretations of substituted benzene π I^v to assume a first benzene π I^v of 9.25 eV, possibly because this is the ionization potential obtained from extrapolation of the benzene vacuum UV Rydberg series. It does not seem to be widely recognized that because of failure of the Born-Oppenheimer approximation in higher Rydberg states, the ionization energies obtained by extrapolation of a molecular Rydberg series is toward the molecular cation in its geometry relaxed ground state, i.e. it is the adiabatic ionization energy which is obtained. There is, therefore, no conflict between the benzene adiabatic 9.25 eV and the well known 9.247 eV ionization energy from the Rydberg series.

A plot of the first π I^{v} against CNDO/2—ϵ_{SCF} yields the least-squares regression (eq. 1), with a standard deviation, s, of 0.06 eV and a correlation coefficient, r^2, of 0.94. Separate regressions for CX_3 (eq. 2, s 0.03 eV, r^2 0.99) and SiX_3 (eq. 3, s 0.06 eV, r^2 0.95) provide a much better correlation for the carbon containing substituents.

$$I^{\mathrm{v}}_{\mathrm{MX}_3} = -0.79 - 0.79\, \epsilon^{\mathrm{CNDO}}_{(a')} \tag{1}$$

$$I^{\mathrm{v}}_{\mathrm{CX}_3} = -0.32 - 0.90\, \epsilon^{\mathrm{CNDO}}_{(c')} \tag{2}$$

$$I^{\mathrm{v}}_{\mathrm{SiX}_3} = 0.47 - 0.82\, \epsilon^{\mathrm{CNDO}}_{(a')} \tag{3}$$

Poorer correlations are found with CNDO/2′ calculations which omit the Si 3*d* functions and with second I^{v}.

It is only through the approximation of Koopmans' theorem [5], of course, that the vertical ionization energies may be identified with minus the SCF molecular orbital energies, $-\epsilon_{\mathrm{SCF}}$. The error in Koopmans' theorem lies in the neglect of electron reorganization in the radical cation and differences in electron correlation energy between the neutral molecule and the radical cation. There are at least two conditions where significant failures of Koopmans' theorem are likely. First, when the positive charge of the radical cation is highly localized, and secondly when the cation is substituted by a highly polarizable group. The successful correlation of I^{v} with $-\epsilon_{\mathrm{SCF}}$ within a series of related molecules relies, therefore, on the correction terms to Koopmans' theorem remaining constant (or small). A requirement of separate correlations for CX_3 and SiX_3 might, for example, reflect the greater polarizability of SiX_3 as compared to CX_3.

Within the experimental results, Table 1, certainly the low first I^{v} of $M(OCH_3)_3$ substituted benzenes, as well as the opposite effects of $C(OCH_3)_3$ and $Si(OCH_3)_3$ on the second I^{v} seem unexpected. The modified CNDO/2 calculations, which include *d* orbitals, do a remarkable job then in predicting correctly the observed order of increasing first I^{v} in $C_6H_5MX_3$ for all substituents. It should be, therefore, worth examining these substituent effects within the framework of the calculations to see in what way they can be related to traditional models of organic chemistry.

First order perturbation theory may be applied to the final Hartree—Fock CNDO/2 matrix to obtain the combined inductive-field effects of MX_3 on the *j*th benzene molecular orbital energies. The inductive-field effect on molecular orbital j energy, $\delta\epsilon_j^{IF}$, is given by eq. 4 where C_{ij} is the atomic orbital coefficient of orbital i in the j molecular orbital, and δf_{ii} is the change in the diagonal element of the HF matrix on substitution. The summation is taken over all atomic orbitals contributing to the j molecular orbital.

Values of δf_{ii} and $\delta\epsilon_j^{IF}$ (a', a'') from calculations including *d* orbitals for Si (and Cl) are collected in Table 2 along with $\delta\epsilon$ (a', a'') and δI^{v} (a', a''). The difference, $\delta\epsilon - \delta\epsilon^{IF}$ is a measure of resonance effects as they enter the calculation.

$$\delta\epsilon_j^{IF} = \sum_{i}^{AO} C_{ij}^2\, \delta f_{ii} \tag{4}$$

The changes in δf_{ii} on MX_3 substitution may in turn be expressed by eq. 5 where the atomic orbital i is on atom A and other terms have the following meaning. The P_{jj} represent total electron charge density on atom J; γ_{JK} are the usual one (J = K) and two centered (J ≠ K) atomic orbital repulsion integrals; Z_J is the effective core nuclear charge of atom J. Summations over B ≠ A, S are over all atoms B in the benzene ring. Summations over S are taken over all substituent atoms.

The terms in P_{SS} and P^0_{SS} require some additional explanation.

$$\delta f_{ii} = \delta(P_{AA} - \tfrac{1}{2}p_{ii})\gamma_{AA} + \sum_{B \neq A,S} \delta P_{BB}\gamma_{AB} + \sum_{S \neq A,B} \delta P_{SS}\gamma_{AS} + \sum_{A \neq A,B} (P^0_{SS} - Z_S)\gamma_{AS} - (P_{HH} - 1)\gamma_{A,H_1} \tag{5}$$

The term P^0_{SS} represents the electron-charge density at atom S in the reference non-interacting substituent, in this case MX_3. The choice of this reference charge density is arbitrary, but since we would like the fourth term in eq. 2 to represent a field effect in the absence charge donation to or from the substituent, an appropriate choice of P^0_{SS} terms would be those from the charge-density distribution in the substituent dimer X_3MMX_3. The terms in δP_{SS} constitute a small correction then to the field effect as the result of substituent atom charge density changes on union with the benzene ring. It is somewhat arbitrary as to whether this third term in eq. 5 is to be regarded as part of the substituent field or inductive effect. It seems more consistent to this author to regard the first three terms of eq. 5 as the net inductive effect of the substituent and the fourth term taken alone as the substituent field effect. Note that the inductive effect (terms 1, 2 and 3) in eq. 5 includes both σ and π contributions to changes in charge density at atom A. The inductive effect is, therefore, $I_\sigma + I_\pi$.

TABLE 2

CHANGES (δ) IN $C_6H_5MX_3$ BENZENE CARBON $2p_z$ HARTREE—FOCK ELEMENTS (f_{ii}), CALCULATED EIGENVALUES, NAD OBSERVED IONIZATION ENERGIES (eV)

MX_3	CH_3	SiH_3	CF_3	SiF_3	CCl_3	$SiCl_3$	$C(OCH_3)_3$	$Si(OCH_3)_3$
δf_1	0.15	−0.01	−1.33	−1.22	−0.87	−0.76	−0.11	0.58
$\delta f_{2(6)}$	−0.15	0.10	−0.54	−0.37	−0.53	−0.21	−0.10	0.41
$\delta f_{3(5)}$	0.14	−0.21	−0.50	−0.83	−0.35	−0.59	0.09	0.14
δf_4	−0.03	−0.01	−0.40	−0.41	−0.35	−0.29	−0.01	0.24
$\delta\epsilon^{IF}a'$	0.04	−0.02	−0.75	−0.74	−0.55	−0.48	−0.04	0.36
$\delta\epsilon\, a'$	0.38	−0.22	−0.59	−1.03	−0.14	−0.65	0.26	0.28
$-\delta I^{V}a'$	0.43	−0.21	−0.8	−0.8	0.00	−0.14	0.29	0.36
$\delta\epsilon^{IF}a''$	0.00	−0.05	−0.52	−0.60	−0.44	−0.40	−0.01	0.28
$\delta\epsilon\, a''$	0.02	−0.10	−0.55	−0.70	−0.44	−0.50	0.02	0.25
$-\delta_{I}{}^{V}a''$	0.00	0.07	−0.43	−0.51	−0.3	−0.4	−0.06	>0.1

The last term in eq. 5 is constant, containing the change in A, H(1) electron repulsion due to the removal of the H at C(1) and MX_3 substitution of benzene.

Beginning with the CNDO/2-calculated changes in f_{ii} of Table 2, several generalizations are possible. Taking the difference $(\delta\epsilon - \delta\epsilon^{IF})$ as a measure of substituent resonance effects within the calculation and comparing this with observed δI^v, as would be expected from the nodal character of the a' orbital at the substituent site, IF terms determine the direction and magnitude of the calculated MX_3 substituent effect on the a'' benzene I^v. A particular feature of interest is the large IF effect of $Si(OCH_3)_3$ which decreases the I^v, whereas exactly the opposite effect is predicted and observed for $C(OCH_3)_3$. The IF effects of CH_3 and SiH_3 are predicted to be small but in opposite directions.

The qualitative features of the origin of the substituent IF effects are to be found in Table 3 and 4 and a consideration of the terms in eq. 2. In Tables 3 and 4, δP_{ii} is the change in electron density at carbon i; $Q(M)$ and $Q(X_3)$ are the net charges $(P_{SS} - Z_S)$ at M and X_3. The difference δQ_S is the electron density donated to the benzene ring by the substituent MX_3.

There is a noticeable tendency toward charge alternation on the carbon atoms of $C_6H_5MX_3$ which increases as M becomes more positive. The charge at C(1) is, therefore, an unreliable indication of the net inductive effect of MX_3 especially where $Q(M)$ exceeds +0.5. This appearance of charge alternation in response to an adjacent center of positive charge is a feature the CNDO/2 calculation shares with ab initio results [8]. There is, however, no first order correction to ϵ_i if the charge redistribution takes place entirely within the atoms contributing to the molecular orbital, i.e. if charge is arbitrarily redistributed within a MO; there is an internal cancellation of the first two terms in eq. 2. The direction of the inductive effect of MX_3 is best provided by δQ_S which is the net electron density donated to the benzene ring. (Differences between δQ_S and ΣP_{ii} are due to electron redistribution at ring H atoms).

Substituents MH_3 and $M(OCH_3)_3$ are net electron donating. Substituents MF_3 and MCl_3 are electron withdrawing. If the electron density changes of $C_6H_5SiX_3$ are divided into σ and π effects some interesting additional features emerge. All of the SiX_3 substituents are strongly σ-electron donating, ranging from +0.09 ($SiCl_3$) to +0.15 ($Si(OCH_3)_3$) units of electron density. Opposing this $+I\sigma$ effect

TABLE 3

CHARGE DISTRIBUTION (Q) AND CHANGES IN ELECTRON DENSITY (δP) AS CALCULATED BY CNDO/2 WITH d-ORBITALS

MX_3	CH_3	SiH_3	CF_3	SiF_3	CCl_3	$SiCl_3$	$C(OMe)_3$	$Si(OMe)_3$
δP_{11}	−0.07	0.13	0.02	0.19	−0.04	0.13	−0.02	0.13
δP_{22}	0.03	−0.05	−0.02	−0.08	0.00	−0.06	0.02	−0.03
δP_{33}	−0.01	0.01	−0.00	0.02	−0.01	0.01	−0.01	0.01
δP_{44}	0.02	−0.02	−0.02	−0.05	0.00	−0.04	0.01	−0.01
$\sum_1^6 \delta_{ii}$	−0.01	0.04	−0.04	0.02	−0.06	−0.01	0.02	0.09
$Q(M)$	−0.06	0.49	0.72	1.21	0.26	0.60	0.44	0.51
$Q(X_3)$	0.07	−0.45	−0.78	−1.23	−0.34	−0.66	−0.41	−0.38
δQ_S	0.01	0.04	−0.06	−0.02	−0.08	−0.06	0.03	0.13

TABLE 4

CHARGE DISTRIBUTION (Q) AND ELECTRON DENSITY CHANGES (δP) AS CALCULATED BY CNDO/2′

MX_3 ~~SiH~~	SiH_3	SiF_3	$SiCl_3$	$Si(OCH_3)_3$
$\sum_{1}^{6} \delta P_{ii}$	0.10	0.14	0.07	0.17
$Q(M)$	0.52	1.77	0.92	1.19
$Q(X_3)$	−0.39	−1.66	−0.86	−1.00
δQ	0.13	0.11	0.06	0.20

is a $-I\pi$ electron-withdrawing effect of approximately the same magnitude due to the vacant Si 3*d* orbitals in the basis set. This "*d* orbital" effect in the calculations is clearly revealed in the Table 4 when the calculations are carried out omitting "*d* orbitals". The d_{yz} orbital mixing coefficients in the a' π orbitals are of the magnitude 0.17, which is excessive as stated previously, and the magnitude of any Si $-I_\pi$ (electron withdrawing) effect must therefore be overestimated. The consequences of opposing inductive and field effects in interpreting organometalloid substituent effects on reactions are important and should be experimentally verifiable. Unfortunately there have been few investigations of substituent effects or linear free energy relationships in Group IV organometalloid chemistry analogous to those carried out for carbon.

Electron charge stabilizing and cation destabilizing field effects of MF_3, MCl_3, and SiH_3 are created by the large electron charge displacement towards X which develops when M is substituted by more electronegative atoms (Tables 3 and 4). This field effect in MF_3 and MCl_3 substituents should increase in the order C < Si < Ge < Sn as the central metal becomes more electropositive, which accounts for the relative substituent effects of $SiF_3 > CF_3$ and $SnCl_3$ on $> SiCl_3$ on increasing the a'' I'. Some caution is necessary in focusing only on the positive charge at M, however, since the two-center electron repulsion integrals (eq. 5) will also decrease in the order C > Si ~ Ge > Sn. In cases, for example, where the charge at C and Si are comparable, the field effect of CX_3 would be greater than SiX_3.

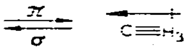
In the CNDO/2 calculation, the $Si(OCH_3)_3$ substituent field effects (eq. 5) on the a' and a'' π orbitals are dominated by a large negative charge at the oxygen atoms (−0.28 per oxygen). Qualitatively, the same description of the field effect is obtained from consideration the $Si{\equiv}(OCH_3)_3$ net bond dipole moment which is directed toward the benzene ring in the calculation. The calculated field effect on the a' π orbital is slightly greater than upon the a' orbital, which experiences an inductive effect in the same direction. As a result, the net $Si(OCH_3)_3$ substituent *IF* effect is to increase the a' and a'' π orbitals by nearly the same energy. Thus, the $Si(OCH_3)_3$ field effect is the opposite of MCl_3, MF_3 and also $C(OCH_3)_3$ in the CNDO/2 model.

The result of removing the *d* orbitals in the CNDO/2′ calculation is to reverse the field effect of the $Si(OCH_3)_3$ group, and the small net *IF* effect is determined by a large σ-electron releasing inductive effect. Agreement between CNDO/2′ results and experiment is poor, although the assignments remain the same with

a' π at highest energy. Although the calculation was not performed, presumably there would be better agreement of the CNDO/2′ calculation with experiment if the $C_{3}v$ geometry IV was assumed. This geometery will minimize the cation destabilizing field effect.

In the C_3 geometry chosen for methyl orthobenzoate, a calculated small electron donating character for $C(OCH_3)_3$, about two-thirds π, is opposed by a slightly greater field effect resulting in small decreases in the energies of both a' and a'' π orbitals. The net charge density at each oxygen (—0.26 e) makes the oxygen contributions to the orbital field effects comparable but slightly greater than those of the positive central carbon, producing a small field effect whose direction in the end is sensitive to the position of the methyl groups. In any case, the experimental result of a small increase in the second I^{v} relative to benzene is in agreement with the model of small and opposing inductive and field effects for the $C(OCH_3)_3$ substituent and the benzene π-orbital energies. The origin of the $C(OCH_3)_3$ π-electron donation will be treated shortly.

The inductive and field effects of the MX_3 substituents as qualitatively described by the CNDO/2 calculation may be summarized by the structures V through XII below; inductive effects are indicated by →, field effects by →.



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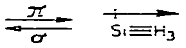

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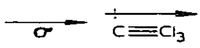

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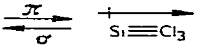

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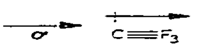

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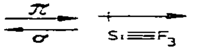

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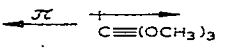

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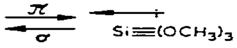


(XII)

It only remains to examine the resonance effects ($\delta\epsilon - \delta\epsilon^{IF}$) of MX_3 as they appear in the CNDO/2 calculations and to decide to what extent the indicated assignments may be correct.

To obtain the most accurate PES spectrum of phenylsilane relative to benzene in the 9.0 to 10.0 eV range, consecutive spectra benzene, phenylsilane, benzene were run as quickly as commensurate with good spectra over this limited range to minimize instrumental drift in calibration. The most intense and sharp vibrational components of both benzene and phenylsilane first I^{v} are coincident at 9.25 eV within the limits of this experiment (±0.02 eV). Further, above 9.25 eV the band shapes are congruent. Below 9.25 eV at 9.14 eV the spectrum of phenylsilane exhibits a slightly weaker adiabatic component which is part of a 3-membered 0.1 eV vibrational progression in the phenylsilane PE spectrum. Resolution (0.02 eV) was not sufficient to tell if the 0.1 eV progression in the silane is in fact similar to the progression as found in benzene [6], but it is interesting to note that a number of weak PES maxima, one of which lies at 9.15 eV in the benzene PES spectrum, have been assigned [6] to hot bands by analogy with similar bands in the Rydberg UV spectra.

The CNDO/2 and CNDO/2′ calculations provide different assignments for the first two I^{v} of phenylsilane and conflicting descriptions of the SiH_3 group. In the CNDO/2 model, two way charge transfer leaves the SiH_3 group as a weak electron-donating substituent with a compensating field effect in the opposite direction, but it is Si p—d π bonding which decreases the energy of the a' π orbital below that of the a'' orbital. In the CNDO/2 model there is no evidence of silicon hydrogen hyperconjugation into the a' π molecular orbital.

With the omission of Si $3d$ orbitals from the basis set, the SiH_3 group emerges as a strong electron donor; and by contrast with the CNDO/2 model, there is now some SiH hyperconjugation, all contributing to a decrease in the a' I^v. (The Si $3p_z$ AO mixing coefficient in a' π is 0.091.) There is, as a result, a calculated decrease in both the a'' π I^v. By way of comparison the CH_3 group is described in the CNDO/2 model as a very weakly electron donating, almost no field effect and as interacting almost entirely by a C—H hyperconjugation reaction. If the extremes of the two CNDO/2 models are regarded as bracketing some "true" description of the SiH_3 group, a satisfactory description of the SiH_3 group would probably be one of a nearly net zero inductive-field effect and a very small SiH hyperconjugating ability. Thus, hyperconjugation only models [9], which have been successful in comparing the PE spectra of SiH_3 and CH_3 substituted alkenes and alkynes, seem very reasonable. The close correspondence between the benzene and phenylsilane PE spectra, and the above arguments, suggest that the envelope of the first PE band in the spectrum of phenylsilane may well represent the "pseudo" Jahn—Teller splitting of an accidental near degeneracy of the $^2A'$ and $^2A''$ cation states. Certainly no conclusion regarding d orbitals are justified from the results.

In the halogenated substituents $SiCl_3$ and SiF_3, the resonance effects of any $p - d$ π back bonding to silicon serve to improve the correlation between observed and calculated I^v but do not determine the magnitude or direction of the substituent effect.

With or without d orbitals, however, in the basis functions, the observed trichlorosilylbenzene first I^v deviates significantly from the regressions (I) and (III) by 0.13 to 0.14 eV. Substitution of trichlorosilylbenzene in the *para* position by a methoxyl group should move the ionization associated with the a' π orbital to lower energy while leaving the a'' π orbital energy relatively unchanged; the observed ionization energies of anisole and 1-trichlorosilyl-4-methoxybenzene (Table 1) indicate that contrary to all expectations the a' π I^v of trichlorosilylbenzene is less than its a'' π I^v; it is the 9.7 eV I^v which remains at 9.61 eV on *para*-methoxyl substitution rather than the 9.46 eV I^v which moves to 8.75 eV and therefore must be assigned to a'.

The molecular orbital calculations do little to suggest an origin for this unexpected order of I^v $a' < a''$, except that in the a' π-molecular orbital significant chlorine p atomic orbital mixing coefficients both including (p_y 0.176) and excluding d orbitals (p_y 0.095, p_z 0.176) along with silicon $2p_z$ coefficients (0.041, 0.051) indicate that some stabilization of the $^2A'$ radical cation may take place by combination of silicon—chlorine bond hyperconjugation and carbon to chlorine-1,3 $p - \pi$ bonding with the chlorine lone pair. Such interactions are indicated more strongly in the CNDO/2 calculations on benzotrichloride. The inversion of a' and a'' E_{SCF} as compared to I^v may represent in part at least the failure of Koopmans' theorem as applied to trichlorisilylbenzene.

The PE spectrum of trimethoxysilylbenzene exhibits an intense band with a maximum at 8.96 eV, which is however considerably broadened to the high energy side providing an estimate of 9.2 eV or less for the second I^v (Table 1).

Because this second I^v is not clearly resolved from the first, the results of *para*-methoxy substitution are less obvious than they were for trichlorosilylbenzene in confirming the assignment of the first I^v to a'. It must first be appreciated that both the field and resonance effects of the trimethoxysilyl group on the $^2A'$ state of anisole cation will be somewhat less than that found for the $^2A'$ benzene cation state, because of displacement in anisole of positive charge on to the methoxyl group. Trimethoxysilyl substituent effects on $^2A''$ states, because of the nodal character at carbons 1 and 4, should remain nearly the same in anisole and benzene. This may explain the nearly equal trimethoxysilyl substituent (as well as trichlorosilyl) effects on the a' and a'' π I^v of anisole (Table 1). In any case, sufficiently satisfactory correlations exist between the 1-trimethoxysilyl-4-methoxybenzene a' (8.34 eV) and a'' (9.17 eV), and the 8.96 and the estimated 9.2 ionization energies of trimethoxysilylbenzene to accept the calculated assignments of the latter as a' and a'' respectively.

The silicon *d* orbital resonance effect which decreases ϵ_{SCF} a' is smallest among SiX_3 for the trimethoxysilyl group, and it has already been pointed out that the trimethoxysilyl group is only slightly π-electron withdrawing, by 0.0215 e. In fact in the absence of *d* orbitals according to the CNDO/2′ model the trimethoxysilyl group is even very slightly πelectron donating 0.0012. Within the CNDO/2 calculation, the oxygen $2p_y$ function appears in the a' π-molecular orbital with a mixing coefficient of 0.118 which suggests some small 1,3 $p - \pi$ interaction between the benzene ring and the oxygen lone pair electrons contributing to the stabilization of the $^2A''$ radical cation in addition to the previously observed field effect. Small silicon p_z (0.040) and oxygen p_z (0.006) coefficients preclude an important silicon oxygen hyperconjugation to the a' π molecular orbital.

Of course heteroatom, $\ddot{X}$, p_y atomic orbital mixing coefficients of the magnitude 0.1 do not of themselves require that the 1,3 $p - \pi$ interaction has had a significant effect on the a' π benzene orbital energy. It is necessary to also consider corresponding off diagonal elements of the final SCF Hartree—Fock matrix which are of the magnitude of 5 eV for adjacent carbon $2p_z$, 0.3 eV for the 1,3 $p - \pi$ interactions in $PhSiX_3$ between phenyl Cl and X-$2p_y$, and 0.8 eV for $PhCX_3$ 1,3 $p - \pi$ interactions, when X is Cl or CH_3O.

The change in a' π energy of the benzene orbital due to a 1,3 $p - \pi$ perturbation by an X (p_y) orbital is given by the general expression (eq. 6) where ϵ_i and ϵ_j represent the difference in benzene a' π and X(p_y) orbital energies and the product $C_i^2 \cdot C_j^2$ is then equal to 1/3. Since $(\epsilon_i - \epsilon_j)$ is on the order of 1 eV where X is methoxyl and 2 eV where X is chloro, only for $C(OCH_3)_3$ is an increase in a' π orbital energy of the magnitude 0.2 to 0.3 eV expected on the basis of the calculated 1,3 interaction integrals f_{ij}.

$$\delta\epsilon_i = C_i^2 \cdot C_j^2 f_{ij}^2 / (\epsilon_i - \epsilon_j) \qquad (6)$$

Considering the relative success of the CNDO/2 method where compared with the CNDO/2′ model omitting *d* orbitals, the question must arise as to whether the necessity of including *d* orbitals or similar virtual functions into descriptions of bonding of silicon-containing molecules is implied by the results here. Whether in the context of spectroscopic transitions or chemical reactions this question could only be answered satisfactorily by examining the differential effect of these functions in "ab initio" calculations on initial and final states, where the property of interest is determined by a difference in state properties. The semi-empirical calculations can, however, serve as a guide to suggest systems where these "*d*-orbital effects" might be found in more rigorous calculations. For example, inclusion of *d*-type functions may have little effect on the total energy of the neutral molecule trimethoxysilylbenzene, but play a greater role as a polarization function in stabilizing the radical cation.

A more pragmatic use of the results of semi-empirical calculations is also possible, in that the charge distribution as described by the CNDO/2 calculation may be accepted without regard for the role of $3d$ functions in the calculation, and the results safely incorporated as inductive and field effects in simpler, more qualitative models within the limits of their useful accuracy. None of the experimental results reported here require the introduction of d orbitals within the simpler, qualitative models of inductive, field and resonance effects.

Leaving resonance effects in SiX_3 for those in CX_3, hyperconjugation plays a significant role not found in the corresponding silyl substituents. The carbon $2p_z$ atomic orbital mixing coefficient of methyl in the a' π orbital is 0.135 and hyperconjugation accounts for 90% of the decrease in the first I^v of toluene relative to benzene.

It is more surprising to find in the CNDO/2 calculation strong carbon chlorine hyperconjugation which places the a' π orbital of benzotrichloride at higher energy than the a'' orbital. The carbon CCl_3 $2p_z$ orbital appears in the a' benzene π orbital with a 0.134 coefficient, and the chlorine p_z enters with a 0.166 AO mixing coefficient. Support for this interaction is apparently indicated by ^{19}F NMR determinations [10] of Taft—Hammett σ^0 values for the series $FC_6H_4CH_nCl_{3-n}$ (n is 0 to 3) in which the absence of significant increases in σ^0 from n equals 1 to zero was interpreted as evidence of possible back π-electron donation to the benzene ring by the trichloromethyl group.

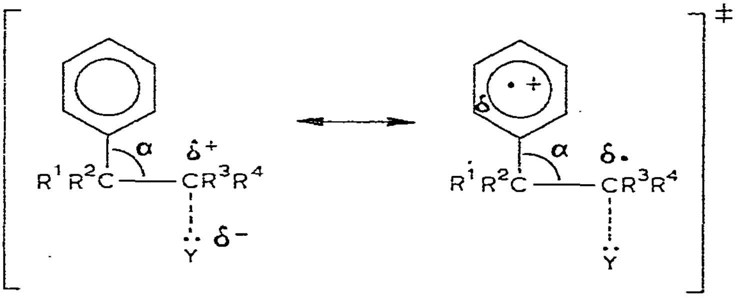
There is also a small through space 1,3 $p - \pi$ interaction in the benzotrichloride as indicated by a chlorine p_y contribution of 0.0734 to the a' π orbital, but there is a relatively large energy gap of greater than 2 eV between the chlorine lone pair and the a' and a'' π-orbital energies which tends to reduce the importance of this through space interaction, as previously mentioned.

The oxygen lone pair electron I^v of methylorthoformate (10.23 and 10.60 eV) are significantly closer to the benzene degenerate π-orbital energies (9.32 eV), and the resonance effect of the $C(OCH_3)_3$ group which accounts for a 0.3 eV stabilization of the benzene radical cation relative to the neutral molecule has a different origin from that of the trichloromethyl group. It is the oxygen $2p_y$ atomic orbital coefficients, not the carbon $2p_z$, which now have significant mixing coefficients (0.122) in the a' π-orbital. The increase in the a' π-orbital energy of methylorthobenzoate is described as the result of a 1,3 $p - \pi$ interaction between the π-orbitals of the benzene ring and the highest filled symmetry adapted group orbital of the three oxygen $2p_y$ lone pair electrons. If the I^v is taken as the difference in energy between radical cation and neutral molecule ground states having identical geometries, the decrease in I^v may be regarded as an intramolecular charge transfer stabilization of the radical cation relative to the neutral molecule as indicated in structure XIII. It is this interaction which accounts in the CNDO/2 model for the π-electron charge donating effect of the $C(OCH_3)_3$ group.

(XIII)

Again, experimental support for the interpretation given to the PE results is also found in the small but significant negative Taft—Hammett σ_I^0 and σ_R^0 values determined from the ^{19}F NMR studies of Sheppard [10] on substituted fluorobenzenes. There is additional significance to this experimental confirmation of the 1,3 through space $p - \pi$ interaction in substituted benzene.

The observation of linear correlations between solvolysis rate constants of β-phenylalkyl derivatives and the ionization energies of substituted benzene has in the past prompted this author to suggest an unsymmetrical cation transition state XIV for these reactions, which was stabilized by intramolecular charge transfer or 1,3 $p - \pi$ interactions between the benzene π ring and the developing carbon 2*p* orbital at the carbonium ion center [11]. The magnitude of this interaction would depend on the indicated angle α which in turn would vary from 109° to just over 60° as a function of R^1, R^2, R^3 and R^4, the leaving group Y, and the solvent.



(XIV)

The observation of 1,3 $p - \pi$ or intramolecular charge-transfer interactions in methylorthobenzoate where the angle α is 109° must support quite strongly the same interaction in the transition state XIV where the angle α must often be considerably smaller than this.

An earlier failure of Eaton and Traylor [12] to observe similar 1,3 $p - \pi$ interactions in molecules of the form $\ddot{G}—CH_2CH{=}CR_2$, where G is, for example, CH_3S or *p*-anisyl, may lie in an unfavorable geometry assumed by the neutral molecules in their ground state. In the methylorthobenzoate, because of the local threefold symmetry of the $C(OCH_3)_3$ group, the benzene ring is unable to escape interaction with the oxygen lone pair electrons. The transition state XIV, of course, may be relied upon to assume the indicated geometry which maximizes the 1,3 $p - \pi$ stabilization, especially where the reaction proceeds through a phenonium ion intermediate.

Experimental

Photoelectron spectra were determined at Institute for Inorganic Chemistry, University of Frankfurt, on a Perkin—Elmer model 16 photoelectron spectrometer with a heated inlet. Spectra were, in general, calibrated against internal argon after first calibrating the spectrometer against argon and methyl iodide. Some spectra were also calibrated against a double internal standard of xenon and argon. The two methods gave comparable results.

Calculations were carried out on the UNIVAC 1108 at the computer center of the University of Frankfurt. Molecular geometries or standard bond angles and distances were taken from ref. 13.

Compounds reported are all previously known and were either purchased commercially, made available by the research group of Professor Hans Bock, or synthesized by straightforward methods from the literature. Before measuring the PE spectra, compounds were purified by distillation, with careful exclusion of air and moisture where necessary.

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