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σ–π CONJUGATION IN GROUP IVA COMPOUNDS OF INDENE AND INDANE

P. E. RAKITA*, M. K. HOFFMAN**, M. N. ANDREWS and M. M. BURSEY***

Venable and Kenan Chemical Laboratories, University of North Carolina, Chapel Hill, North Carolina
27514 (*U.S.A.*)

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SUMMARY

A series of indanyl and indenyl derivatives of silicon and tin has been prepared and the molecular ionization potentials determined by electron impact mass spectrometry. Substitution of the hydrogen at C(1) by an organosilicon group results in a decrease of the ionization potential by ~0.6–0.8 eV, while extension of the π-system into the five-membered ring via the double bond produces a further decrease of the ionization potential by ~0.2–0.3 eV. The results are consistent with the postulate of a σ–π hyperconjugative interaction between the β metal–carbon bond and the aromatic π-system.

INTRODUCTION

It has been generally established that the σ-electrons in a carbon–metal bond located β to an unsaturated grouping (*e.g.* olefin or aromatic) can exert a significant effect on the electronic structure of the molecule and its chemical reactivity. Bock[1,2] has studied the ionization potentials (*IP*'s) of a variety of phenyl and benzyl silanes by charge-transfer (CT) spectra and mass spectrometry (MS). From the observed lowering of the *IP* (and, hence, raising of the highest filled MO) upon β-substitution of a trimethylsilyl group, it was inferred that a σ–π hyperconjugative interaction was present between the benzene π-system and the β carbon–silicon σ-bond. Traylor[3] and Pitt[4] have demonstrated that the extent of σ–π interaction is markedly dependent on the dihedral angle (θ) between the C–M bond and the π-system, being at a maximum when θ is zero. This conformational requirement has also been invoked in studies of the acid cleavage of allylmercuric halides[5] and ESR studies of radicals containing tin, phosphorous, and arsenic[6].

We have determined the molecular ionization potentials by electron-impact mass spectrometry for a series of indanyl and indenyl derivatives of silicon and tin. In this system, substitutions and variations could be made on the basic molecular

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[*] To whom correspondence should be addressed.

[**] Present address: Department of Chemistry, Kansas State University, Manhattan, Kansas 66502 (U.S.A.).

[***] Fellow of the Alfred P. Sloan Foundation, 1969–present.

framework in a systematic and controlled manner. In particular, the dihedral angle (θ) could be constrained to a value suitable for effective σ–π interaction. By use of the electron impact method of *IP* measurement, we were able to include the stannyl derivatives which could not be studied[4] by the charge-transfer method.

EXPERIMENTAL

General

Unless otherwise indicated, all manipulations were carried out in an atmosphere of dry nitrogen or *in vacuo*. Infrared spectra were recorded on liquid films between NaCl plates using a Perkin–Elmer 421 Grating Spectrometer. NMR spectra were obtained at 60 MHz utilizing a Jeolco C60-HL spectrometer. Cyclohexane was used as an internal reference. All compounds were purified by VPC prior to measurement. Elemental analyses were performed by Meade Microanalytical Laboratory, Amherst, Massachusets.

Gas chromatographic separations and purifications were carried out using a Hewlett–Packard Model 5750 or a Varian Aerograph Model 90-P3 Chromatograph equipped with thermal conductivity detectors. Columns (1/4″ × 26″ and 1/4″ × 60″) packed with 15% SE-30 on Chromosorb W were employed using helium elution. Typical separations were carried out at 150° and a flow rate of 30 ml/min.

Preparation of samples

Indene was obtained commercially and purified by VPC. Samples of 1-(trimethylsilyl)indene[7], 1-(dimethylphenylsilyl)indene[8], 1-(trimethylstannyl)indene[7], and 1,2-bis(trimethylsilyl)indene[8] were prepared as described in the literature. Indane was obtained by the catalytic hydrogenation of indene and purified by distillation followed by VPC.

Preparation of 1-(*trimethylsilyl*)*indane*

A solution of 1-(trimethylsilyl)indene (1.88 g, 0.01 mol) in ethanol (100 ml) containing 10% Pd/C (0.10 g) was stirred in an atmosphere of hydrogen at room temperature until consumption of gas ceased. The reaction was complete within one hour with a total uptake of hydrogen equivalent to one mole per mole of 1-(trimethylsilyl)indene. The mixture was filtered to remove the catalyst and the solvent was removed under reduced pressure at room temperature. The residue was purified by VPC to obtain 1-(trimethylsilyl)indane. (Found: C, 76.09; H, 9.68; $C_{12}H_{18}Si$ calcd.: C, 75.72; H, 9.53%.)

The proton NMR spectrum (CCl_4) had the following resonances: τ 2.2–3.1 (multiplet, 4H), 6.8–8.1 (multiplet, 5H), 9.98 ppm (singlet, 9H). Infrared bands were seen at: 3067 w, 3020 w, 2954 s, 2900 w, 2874 m, 1713 w, 1595 w, 1470 m, 1450 w, 1435 w, 1400 vw, 1255 (sh), 1242 vs, 1195 w, 1100 w, 1080 vw, 1019 vw, 1004 vw, 989 vw, 927 vw, 900 (sh), 878 m, 857 (sh), 830 vs (br), 746 s, 735 (sh), 710 w, 683 m, 605 w cm^{-1}.

Preparation of 1-(*dimethylphenylsilyl*)*indane*

This compound was prepared from the corresponding indene by a manner analogous to that used for the 1-trimethylsilyl derivative. The product was purified by distillation at 112°/0.5 mmHg. (Found: C, 80.24; H, 7.85. $C_{17}H_{20}Si$ calcd.: C, 80.89; H, 7.98%.)

The proton NMR spectrum (CS_2) showed the following resonances: τ 2.7 (multiplet, 5H), 3.1 (multiplet, 4H), 7.5–8.2 (multiplet, 5H), 9.73 (singlet, 3H), 9.76 ppm (singlet, 3H). Infrared bands were observed at: 3066 m, 3017 m, 2950 m, 2875 m, 1600 w, 1471 m, 1455 w, 1427 s, 1257 (sh), 1253 s, 1200 w, 1116 s, 1085 w, 1025 w, 1010 w, 998 w, 935 vw, 880 w, 861 w, 848 m, 831 s, 812 s, 792 m, 768 m, 753 s, 735 s, 700 s cm^{-1}.

Preparation of 1-*(dimethylethoxysilyl)indane*

A solution of 1-(dimethylsilyl)indene (1.0 g, 0.057 mol) in ethanol (100 ml) containing 10% Pd/C (0.10 g) was stirred in an atmosphere of hydrogen at room temperature. After one hour, no net uptake of hydrogen was observed. The reaction mixture was filtered, and the filtrate concentrated under reduced pressure at room temperature. The residue was purified by VPC to obtain 1-(dimethylethoxysilyl)-indane. (Found: C, 71.30; H, 9.35. $C_{13}H_{20}SiO$ calcd.: C, 70.85; H, 9.15%.)

The proton NMR spectrum (CCl_4) exhibited the following resonances: τ 3.0 (multiplet, 4H), 6.44 (quartet, 2H, *J* 7.5 Hz), 7.0–8.0 (complex multiplet, 5 H), 8.89 (triplet, 3H, *J* 7.5 Hz), 9.95 ppm (singlet, 6H).

Infrared bands were observed at: 3065 w, 3020 w, 2960 s (br), 2870 s, 1595 w, 1460 m, 1450 m, 1435 w, 1385 m, 1245 s, 1195 w, 1160 m, 1100 s, 1075 s, 1020 w, 1005 w, 990 w, 940 m, 875 w, 830 s (br), 765 m, 740 m, 675 w cm^{-1}.

The mass spectrum showed the molecular ion ($C_{13}H_{20}{}^{28}SiO$) at *m/e* 220. Other prominent peaks appeared at *m/e* 116 (C_9H_8), 103 ($C_4H_{11}SiO$), 75 (C_2H_7SiO), and 59 (C_2H_7Si).

Preparation of 1-*(dimethylethoxysilyl)indene*

To a reaction flask containing ethanol (100 ml) and 10% Pd/C (0.10 g) and fitted with a gas dispersion tube and condenser was added 1-(dimethylsilyl)indene (1.0 ml). The reaction mixture was stirred for 4 h at room temperature while nitrogen was continuously bubbled though the solution. Additional ethanol was added as needed to maintain the volume. The mixture was filtered, and the filtrate concentrated under reduced pressure at room temperature. The remaining liquid was purified by VPC to obtain 1-(dimethylethoxysilyl)indene. (Found: C, 71.48; H, 8.13. $C_{13}H_{18}SiO$ calcd.: C, 71.50; H, 8.31%.)

The proton NMR spectrum (CCl_4) exhibited the following resonances: τ 2.7 (multiplet, 4H), 3.27 (AB portion of an ABX pattern, 2H, J_{AB} 5.1, J_{AX} 1.9, J_{BX} 1.9 Hz), 6.37 (quartet, 2H, *J* 7.5 Hz), 6.50 (X portion of ABX pattern, 1H), 8.82 (triplet, 3H, *J* 7.5 Hz), 10.10 (singlet, 3H), 10.14 ppm (singlet, 3H).

Infrared bands were observed at: 3060 w, 3020 (sh), 2965 m, 2880 m, 1702 w, 1595 w, 1469 vw, 1452 (sh), 1444 m, 1385 m, 1353 w, 1287 w, 1250 s, 1215 w, 1187 w, 1161 w, 1104 s, 1077 s, 1022 s, 973 w, 944 m, 875 w, 857 w, 832 s, 814 s, 801 s, 772 vs, 752 m, 724 w, 710 m, 689 w cm^{-1}.

Ionization potential measurements

Ionization potentials were measured on a Hitachi RMU-6E mass spectrometer, modified by the incorporation of a digital voltmeter readable to ±0.01 V

(United Systems Corporation, Dayton, Ohio), with reduced trap current (ca. 2 μA) and repeller voltage (< 0.5 V). Details of the experimental technique have been published elsewhere[9,10]. Ionization potentials of the several indene and indane pairs were measured consecutively or simultaneously to minimize experimental error. In all cases, the quoted error limits are statistical standard deviations, not limits of absolute accuracy. This is usually quoted as ±0.2 eV for the mass spectrometric method, though the present variation of the method reproduces the literature ionization potentials of standard compounds to within 0.03–0.10 eV in the range of energies found here. For related pairs of compounds here the relative accuracy is estimated to be about ±0.05 eV[11].

RESULTS AND DISCUSSION

Preparation of compounds

For the silylindenes, catalytic reduction under standard conditions yielded the corresponding silylindanes. However, attempted reduction of 1-(dimethylsilyl)indene using H_2/Pd on C/ethanol gave, unexpectedly, 1-(dimethylethoxysilyl)indane. The product was identified by NMR and mass spectrometry. The NMR spectrum displayed no resonances attributable to vinylic or silyl (Si–H) protons. Instead, a complex multiplet in the region τ 7–8 ppm, characteristic of the protons in the five membered ring of a 1-substituted indane, was observed. Moreover, a quartet (τ 6.44 ppm, 2H) and triplet (τ 8.89 ppm, 3H), typical of an ethoxy group, appeared in the spectrum. Prominent peaks in the mass spectrum at *m/e* 116 (C_9H_8) and 103 ($Si(CH_3)_2OC_2H_5$) as well as the molecular ion [$C_9H_9Si(CH_3)_2OC_2H_5$] at *m/e* 220 confirmed the assigned structure.

The corresponding 1-(dimethylethoxysilyl)indene was obtained by the Pd/C catalyzed solvolysis of 1-(dimethylsilyl)indene in ethanol while the system was continuously purged with nitrogen. The characteristic AB portion of an ABX pattern for the vinylic protons of a 1-substituted indene, the presence of the triplet and quartet of the ethoxy group, and the absence of a signal for the silyl (Si–H) proton establish the structure. The details and scope of these reactions are currently being explored[12].

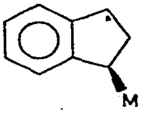
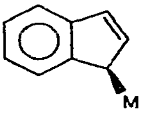
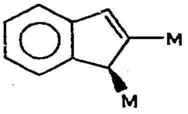
Ionization potential data

Table 1 lists the results obtained in this study (for comparison, values obtained by the CT method from ref. 4 are included.) The values for indane and the various silylindanes display a decrease in the *IP* of 0.18–0.27 eV upon inclusion of the double bond in the five-membered ring. For both the indanes (I) and indenes (II), C(1) substitution by an organosilicon group further lowers the *IP* by 0.6–0.8 eV, differences greater than those observed by the CT method[4]. Within the series (Ib)–(Id) and (IIb)–(IId), the differences due to the silicon substituents are small (within experimental error) and no trend based on the substituents is apparent although the order $OC_2H_5 < CH_3 < C_6H_5$ occurs in both series and the range of values is greater for the indanes (0.13 eV) than the indenes (0.06 eV). The trimethyltin substituent at C(1) lowers the *IP* of both indene and indane to 7.29 eV. Disubstitution in the 1- and 2-positions on the five-membered ring [compound (III)] causes an additional reduction in the *IP* of ~0.1 eV compared with (IIb).

The effects of the C(2)–C(3) double bond and the C(1) substituent on the *IP* are

TABLE 1

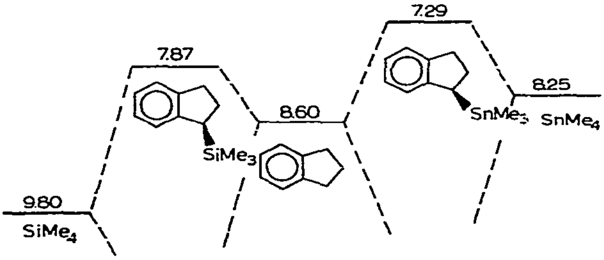
IONIZATION POTENTIALS BY ELECTRON-IMPACT MASS SPECTROMETRY (in eV)

	M			
		(I)	(II)	(III)
(a)	H	8.60±0.01 8.52 (CT)	8.33±0.01	
(b)	$Si(CH_3)_3$	7.87±0.01 8.13 (CT)	7.65±0.01	7.54±0.01
(c)	$Si(CH_3)_2OC_2H_5$	7.81±0.01	7.63±0.01	
(d)	$Si(CH_3)_2C_6H_5$	7.94±0.01	7.69±0.04	
(e)	$Sn(CH_3)_3$	7.29±0.01	7.29±0.01	

qualitatively additive in the case of the silanes but not for the stannanes. No additional lowering of the *IP*, indicative of conjugation throughout the five-membered ring, is apparent in the data.

Discussion

For both the indanes (I) and indenes (II) the ionization potentials decrease for the series M = H > Si > Sn. Although accurate structural data for these compounds are not available, it is reasonable to assume that successive replacement of M with H, Si, and Sn gives rise to only minor structural changes in the rest of the molecule. Other workers[3,4] have convincingly demonstrated that when the C–M bond is constrained to lie in the nodal plane of the π-system (where no σ–π interaction is possible) only minor changes in the *IP*'s (typically ~0.1 eV) are observed for the changes M = C, Si, Ge, Sn. In the systems studied here, the C–M bond is restricted to a dihedral angle of ~35° with the π-system. If, as suggested, structural factors are essentially constant in the series, then the successive decrease in *IP*'s going down the series of Group IVA metals may arise primarily from closer energy matching between the C–M bond and highest occupied π-MO.



It should be noted that for the trimethylsilyl and trimethylstannyl derivatives of both indene and indane, the *IP*'s are lower than the values[13] for tetramethylsilane (9.8 eV) and tetramethylstannane (8.25 eV). In the latter case, for (trimethylstannyl)-indane, the energy of the σ-electrons is presumably higher than that of the π-system (see Figure). Pitt and Bock[14] have recently demonstrated that σ–π conjugation occurs even when the σ-electrons of the substituent are more readily ionized than the π-electrons.

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