CHEMISTRY LETTERS, pp. 1383 - 1384, 1984.

ULTRAVIOLET, CHARGE-TRANSFER, AND PHOTOELECTRON SPECTRA OF PHENYL-SUBSTITUTED GROUP 4B CATENATES, $PhMe_2E\text{-}E'Me_3$ (E = Si, Ge; E' = C, Si, Ge, Sn)[1)]

Hideki SAKURAI,* Michiko ICHINOSE, Mitsuo KIRA, and Teddy G. TRAYLOR[†]
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980
[†]Department of Chemistry, University of California, San Diego, LaJolla,
California 92093, U. S. A.

UV, CT, and PE spectra of eight phenyl-substituted silanes and germanes of the type of $PhMe_2E\text{-}E'Me_3$ (E = Si, Ge; E' = C, Si, Ge, Sn) are recorded. Extensive σ-π conjugation between σ(E-E') and π orbitals is demonstrated to determine the unique electronic structures of these compounds.

In relation to current interests in the photochemistry of phenyldisilanes[2)] and related aryl-substituted Group 4B catenates, we report herein ultraviolet (UV), charge-transfer (CT), and photoelectron (PE) spectral data of some Group 4B catenated compounds. These data will be indispensable to account for the mechanism of the photoreactions of phenyldisilanes and related compounds.

Table 1 shows these spectral data of eight compounds together with some from literature. The CT spectra of tetracyanoethylene (TCNE) complexes with these compounds revealed two bands in which one (band II) had absorption maxima at around 25000 cm^{-1}, and others had those at lower energies depending on the structures. Noteworthy is the fact that the latter bands had extremely low intensities as noted before for phenylpentamethyldisilane.[3)] This means that HOMO of these compounds are composed mainly of σ(E-E') orbitals.[3)] Experimentally, the band maxima were determined by the method of Briegleb.[4)]

In the series of $PhMe_2SiE'Me_3$, both UV (^1L_a) and CT-I band maxima show red-shift as E' changes from C to heavier elements. A similar trend is seen for $PhMe_2GeE'Me_3$. The first ionization potentials calculated from the Voigt-Reid equation,[5)] $\tilde{\nu}_{CT}/eV = 0.83IP/eV - 4.42$, agree quite well with those determined by PE spectra.

Previously, we have observed a linear relationship between UV and CT maxima for benzyl-substituted Group 4B compounds, $PhCH_2E'R_3$ (E' = Si, Ge, and Sn).[6)] Similar linear relations were found also for two series of compounds in this study.

$\tilde{\nu}(^1L_a) = 1.01\tilde{\nu}(CT) + 24500\ cm^{-1}$ (r = 0.996) for $PhCH_2E'Me_3$[7)]
$\tilde{\nu}(^1L_a) = 1.11\tilde{\nu}(CT) + 20400\ cm^{-1}$ (r = 0.999) for $PhMe_2SiE'Me_3$
$\tilde{\nu}(^1L_a) = 1.09\tilde{\nu}(CT) + 21900\ cm^{-1}$ (r = 0.997) for $PhMe_2GeE'Me_3$

Coefficients of almost unity in these relations indicate that ground-state energies are directly reflected to the electronic transitions. However, smaller transition energies in ^1L_a bands of phenylsilanes and phenylgermanes suggest that

Table 1. Spectral data of $PhMe_2E\text{-}E'Me_3$ (E = Si, Ge; E' = C, Si, Ge, Sn)

Compounds	UV(^1L_a)a) $\tilde{\nu}_{max}/cm^{-1}$	 $\varepsilon_{max}/dm^3mol^{-1}cm^{-1}$	CTb)/cm^{-1} I	 II	IP/eV CT	 PE
$PhMe_2SiCMe_3$	46300	9260	23300	25400	8.80	8.79
$PhMe_2SiSiMe_3$	43300	10900c)	20500	25100d)	8.39	8.35e)
$PhMe_2SiGeMe_3$	43200	11800	20600	25300	8.40	8.37
$PhMe_2SiSnMe_3$	41400	11700	18900	25300	8.15	----f)
$PhMe_2GeCMe_3$	46500	8310	22500	25200	8.69	----f)
$PhMe_2GeSiMe_3$	44300	10300	20600	25300	8.40	8.33
$PhMe_2GeGeMe_3$	44000	10600	20400	25300	8.37	8.29
$PhMe_2GeSnMe_3$	42600	12900	18900	25100	8.15	8.20

a) In hexane. b) In dichloromethane with TCNE as an acceptor. c) Ref. 8. d) Ref. 3. e) Ref. 9. f) Not determined.

energy levels of excited states of these compounds are lowered possibly by p-σ^* or $(p\text{-}d)_\pi$ conjugation.10) The fact that three series of compounds gave the same coefficients indicates no extra conjugation such as π^*-d-d.

The first ionization potentials of permethyl Group 4B catenates have been determined by PE spectra (in eV) for $Me_3SiSiMe_3$ (8.69),11) $Me_3SiSnMe_3$ (8.32),12) $Me_3GeGeMe_3$ (8.6),12) $Me_3GeSnMe_3$ (8.33),12) and $Me_3SnSnMe_3$ (8.20).12) We report here additional data for Me_3SiCMe_3 (9.29, PES), $Me_3SiGeMe_3$ (8.65, CT), and $Me_3GeGeMe_3$ (8.59, CT and 8.55, PES). IP values from CT spectra with TCNE as an acceptor are calculated by the Voigt-Reid type equation, $\tilde{\nu}_{CT}/eV = 0.77_1 IP/eV - 3.71_6$, found for permethylpolysilanes.13) Studies on the photochemistry of these phenyl-substituted Group 4B catenates are actively in progress.

References

1) Chemistry of Organosilicon Compounds. 197.

2) inter alia H. Sakurai, J. Organomet. Chem., 200, 261 (1980); H. Sakurai, Y. Nakadaira, M. Kira, H. Sugiyama, K. Yoshida, and T. Takiguchi, ibid., 184, C36 (1980); M. Ishikawa and M. Kumada, Adv. Organomet. Chem., 10, 51 (1981); M. Ishikawa, Pure Appl. Chem., 50, 11 (1978).

3) H. Sakurai and M. Kira, J. Am. Chem. Soc., 97, 4879 (1975).

4) G. Briegleb and J. Czekalla, Z. Phys. Chem., 24, 37 (1960).

5) E. M. Voigt and C. Reid, J. Am. Chem. Soc., 86, 3930 (1964).

6) H. Sakurai, M. Kira, and M. Ochiai, Chem. Lett., 1972, 87.

7) Recalculated from the data of Ref. 6 in addition to those of $PhCH_2CMe_3$.

8) H. Sakurai and M. Kumada, Bull. Chem. Soc. Jpn., 37, 1894 (1964).

9) C. G. Pitt and H. Bock, J. Chem. Soc., Chem. Commun., 1972, 28.

10) For a recent discussion, see J. C. Giordan and J. H. Moore, J. Am. Chem. Soc., 105, 6543 (1983).

11) H. Bock and W. Ensslin, Angew. Chem., Int. Ed. Engl., 10, 404 (1975).

12) L. Szepes, T. Koranyi, G. Naray-Szabo, A. Modelli, and G. Distefano, J. Organomet. Chem., 217, 35 (1981).

13) H. Sakurai, M. Kira, and T. Uchida, J. Am. Chem. Soc., 95, 6826 (1973).

(Received May 23, 1984)