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PRELIMINARY COMMUNICATION

THE ELECTRONIC SPECTRAL PROPERTIES OF TRIMETHYLGERMANECARBOXYLIC ACID AND TRIMETHYLGERMANECARBOXYLATE ION

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We wish to report the novel electronic spectral properties of trimethylgermanecarboxylic acid and trimethylgermanecarboxylate ion in the ultraviolet region. The spectrum of the acid in absolute ethanol shows an absorption maximum λ_{max} 250 mμ (ϵ 572) and a shoulder λ_{max} 254 mμ (ϵ 546), *cf.* Fig.1. The spectrum of the analogous carbon compound, trimethylacetic acid, in absolute ethanol shows an absorption maximum λ_{max} 213 mμ (ϵ 71), the region expected for α-methyl substituted carboxylic acids[1]. The weak absorption maximum in the ultraviolet spectra of aliphatic carboxylic acids in the 210 mμ region, $\epsilon < 150$, is assigned to the $n \to \pi^*$ transition of the carboxyl group[1,2]; Thus, a bathochromic shift of 37 mμ is observed for the carboxyl $n \to \pi^*$ transition of trimethylgermanecarboxylic acid from the transition for the analogous carbon compound. This shift is accompanied by a large increase in the extinction coefficient. For triorganogermanecarboxylic acids with substituent phenyl groups, the $n \to \pi^*$ transition is masked by the phenyl $\pi \to \pi^*$ transition with peaks in the region 247–271 mμ**.

Spectra of saturated aliphatic carboxylate ions show no absorption maximum in the 200–750 mμ region, only a rising end absorption is observed. While the spectrum of sodium trimethylacetate in absolute ethanol is consistent with the above observation, the spectrum of sodium trimethylgermanecarboxylate shows an absorption maximum λ_{max} 254 mμ (ϵ 998) and a shoulder λ_{max} 257.5 mμ (ϵ 890), *cf.* Fig.1. It has been reported that the ultraviolet spectrum of germanecarboxylate ion in ethanol or water consists of a shoulder on the end absorption[3].

The bathochromic shift observed for the carboxyl $n \to \pi^*$ transition of trimethylgermanecarboxylic acid is similar to the bathochromic shift reported for the carbonyl $n \to \pi^*$ transition of α-germyl and α-silyl ketones*** The spectral shift of the carbonyl $n \to \pi^*$ transition has been explained in terms of $(p \to d)\pi$ bonding between the carbonyl group

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**A similar bathochromic shift of the carboxyl $n \to \pi^*$ transition of triorganosilanecarboxylic acids is expected. However, the ultraviolet spectra of only triorganosilanecarboxylic acids with substituent phenyl groups have been recorded to date.

***$\Delta\lambda_{max}$ = 78 mμ for acetyltriethylgermane and $\Delta\lambda_{max}$ = 85 mμ for acetyltrimethylsilane with methyl tert-butyl ketone as the reference compound[4,5]

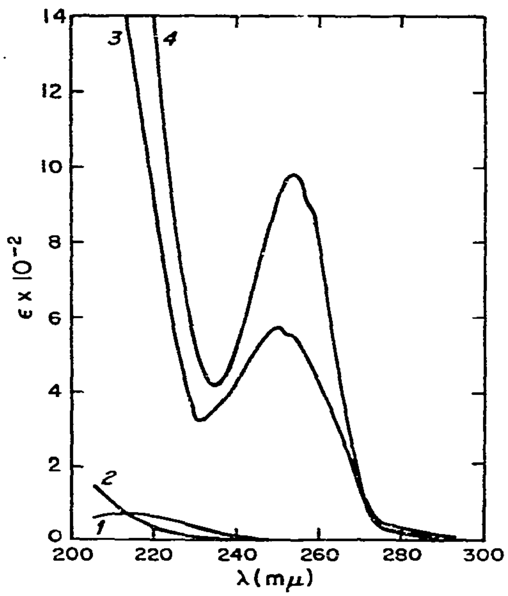

Fig.1. Ultraviolet spectra in absolute ethanol (Cary Model 14 Spectrophotometer): (*1*) trimethylacetic acid; (*2*) sodium trimethylacetate; (*3*) trimethylgermanecarboxylic acid; (*4*) sodium trimethylgermanecarboxylate.

and the vacant *d* orbitals of silicon or germanium, particularly in reference to the excited electronic state, and/or the inductive effect, $+I$, of silicon or germanium[5,6]. The most recent studies favor the inductive explanation with $(p \rightarrow d)\pi$ bonding relegated to a minor role[5,7,8]. The bathochromic shift of the carboxyl $n \rightarrow \pi^*$ transition can be explained in similar terms.

The absorption maximum for the trimethylgermanecarboxylate ion is at a slightly higher wavelength than the maximum for the conjugate acid form★ and the extinction coefficient is larger by a factor of 1.75. The above effects may be an indication of greater participation of the *d* orbitals of germanium in bonding with the π orbital of the CO_2^- group in the trimethylgermanecarboxylate ion than with the carboxyl group in the conjugate acid form. It is expected that there would be a greater demand for charge delocalization by $(p \rightarrow d)\pi$ bonding in the carboxylate anion than in the neutral molecule. The greater acidity of the triorganosilane- and triorganogermanecarboxylic acids than their carbon analogs is in accord with the above proposal★★.

Trimethylgermanecarboxylic acid was prepared by the following procedure. An ether solution of methylmagnesium iodide, 0.53 mole, was added over a period of 3 h to germanium tetrachloride, 0.16 mole, dissolved in tetrahydrofuran. The addition was carried out under a nitrogen atmosphere and the temperature was maintained between 0–5°. Small pieces of lithium wire, 0.58 g-atom, were added and the mixture was stirred for 32 h. After filtration through glass wool, the solvent was removed by

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★Since the ultraviolet spectrum of trimethylacetate ion shows no absorption maximum above 205 mμ, the magnitude of the spectral shift cannot be determined.

★★The order of acidity in 45 wt-% ethanol water, 76 wt-% ethanol–water and dimethyl sulfoxide is, $R_3SiCO_2H \geqslant R_3GeCO_2H > R_3CCO_2H$ (ref. 9).

distillation and the residue was dissolved in anhydrous hexamethylphosphoramide, 60 ml* Small pieces of lithium wire, 0.50 g-atom, were added and the mixture was stirred for 46 h. The dark green solution was filtered through glass wool and poured onto powdered Dry Ice. The Dry Ice slurry was poured directly into a 5% hydrochloric acid solution. The aqueous solution was extracted several times with ether, and the combined ether solution was extracted with a 5% sodium hydroxide solution. After acidification and extraction with ether, the resulting ethereal solution yielded, 4.5 g, 0.028 mole, (17% yield) of the crude acid, Me_3GeCO_2H, on evaporation. Three successive crystallizations from pentane at −78° gave a pure sample. 1.5 g, of trimethylgermanecarboxylic acid, m.p. 26–28° (Found: C, 29.92; H, 6.26. $C_4H_{10}O_2Ge$ calcd.: C, 29.52; H, 6.20).

The infrared spectrum of trimethylgermanecarboxylic acid in carbon tetrachloride is consistent with the proposed structure and shows a carbonyl stretching band at 1642 cm^{-1} as compared with 1693 cm^{-1} for trimethylacetic acid. The shift in the carbonyl stretching frequency of triorganosilane- and triorganogermane-carboxylic acids has been observed previously[11] and is a good criterion for structural conformation**.

Trimethylacetic acid (Eastman Grade) was purified by fractional distillation, b.p. 162.5–163°, m.p. 34–35° (lit.[13] b.p. 162–165° m.p. 34–35°).

REFERENCES

1 A.E. Gillam and E.S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, Arnold, London, 1958, pp.61–62.
2 H.H. Jaffé, D.L. Beveridge and M. Orchin, *J. Chem. Ed.*, 44 (1967) 383.
3 P.M. Kuznesof and W.L. Jolly, *Abstr., 155th Nat. Meeting Am. Chem. Soc., San Francisco, Calif., April 1968*, No. M133.
4 A.G. Brook, J.M. Duff, P.F. Jones and N.R. Davis, *J. Amer. Chem. Soc.*, 89 (1967) 431.
5 F. Agolini, S. Klemenko, I.G. Csizmadia and K. Yates, *Spectrochim. Acta*, 24A (1968) 169.
6 D.F. Harnish and R. West, *Inorg. Chem.*, 2 (1963) 1082.
7 R.W. Harrison and J. Trotter, *J. Chem. Soc.*, A (1968) 258.
8 A.G. Brook, D.G. Anderson, J.M. Duff, P.F. Jones and D.M. MacRae, *J. Amer. Chem. Soc.*, 90 (1968) 1076.
9 O.W. Steward, H.W. Irwin, R.A. Gartska and J.O. Frohliger, *Abstr. 154th Nat. Meeting Am. Chem. Soc., Chicago, Ill., Sept. 1967*, No. 0115; O.W. Steward, J.E. Dziedzic and J.O. Frohliger, *Abstr. 156th Nat. Meeting Am. Chem. Soc., Atlantic City, N.J., Sept., 1968*, INOR 118; O.W. Steward, H.W. Irwin, R.A. Gartska and J.O. Frohliger, *J. Chem. Soc., A*, in press.
10 E.J. Bulten and J.G. Noltes, *Tetrahedron Letters*, (1966) 4389; *ibid.*, (1967) 1443.
11 A.G. Brook and H. Gilman, *J. Amer. Chem. Soc.*, 76 (1954) 77; H. Gilman and W.J. Trepka, *J. Org. Chem.*, 25 (1960) 2201.
12 A.G. Brook, M.A. Quigley, G.J.D. Peddle, N.V. Schwartz and C.M. Warner, *J. Amer. Chem. Soc.*, 82 (1960) 5102; G.J.D. Peddle, *J. Organometal. Chem.*, 5 (1966) 486.
13 S.V. Puntambeker and E.A. Zoellner, *Org. Syntheses*, 8 (1928) 104.

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*For the preparation of trialkylgermyllithium in hexamethylphosphoramide, *cf.* ref. 10.

**A similar shift in the carbonyl stretching frequence has been reported for α-silyl and α-germyl ketones and has been explained on the basis of inductive effects[12]