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SYNTHESIS AND CHARACTERIZATION OF TETRAKIS(2,6-DIETHYLPHENYL)DIGERMENE

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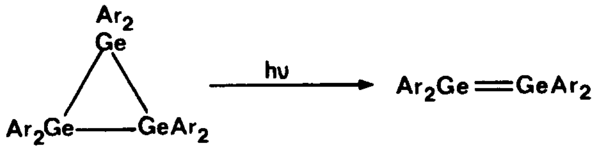
Tetrakis(2,6-diethylphenyl)digermene (1b) has been synthesized and its molecular structure determined: (1) the Ge=Ge bond length is 2.213(2) Å and (2) the molecule has a twist angle of 11° about the Ge=Ge bond and an out-of-plane bending angle of 15° at the germanium atoms.

Digermenes have been implicated as reactive intermediates in several reactions,[1] but it was only in 1982 that *solution* spectra of a digermene, tetrakis(2,6-dimethylphenyl)digermene (1a), were recorded.[2] Compound 1a formed upon photolysis of hexakis(2,6-dimethylphenyl)-cyclotrigermane (2a), but the slow photolytic conversion of 2a to 1a and concomitant photo-induced polymerization of 1a prevented the isolation of this digermene in pure form. This problem has now been solved through use of the corresponding hexakis(2,6-di*ethyl*phenyl)cyclotrigermane (2b) which undergoes exceptionally clean photolytic conversion to provide the title compound (1b). Recently, Lappert and coworkers have reported the synthesis and structural characterization of another digermene [3: $R_2Ge{=}GeR_2$ with $R{=}CH(SiMe_3)_2$][3] which, in contrast to 1b, dissociates to the corresponding singlet germylene in solution.[3a] Thus, this Note describes the first molecular structure of a digermene which retains its double bond in solution as well.



2a,b 1a,b

a: Ar= 2,6-dimethylphenyl
b: Ar= 2,6-diethylphenyl

The synthesis of 1b followed the previously reported procedure.[2] Thus, after the slow addition of bis(2,6-diethylphenyl)germanium dichloride (1.85 mmol) in dimethoxyethane (DME, 2 mL) to a solution of lithium naphthalenide [prepared from naphthalene (4.07 mmol) in DME (4.8 mL) and lithium powder containing 5% Na (4.7 mg atom) at -78°C], the resulting mixture was stirred at the same temperature for 1.5 h and then warmed to room temperature. The product, mp 247-249°, obtained in 29% yield exhibited spectral properties consistent with the formulation of **2b** for this compound: ^1H NMR (250 MHz, C_6D_{12}) δ 0.43 (t, 18H, J=7.4 Hz), 0.55 (t, 18H, J=7.4 Hz), 2.29 (dq, 6H, J=14.8 Hz, 7.4 Hz), 2.60 (dq, 6H, J=14.8 Hz, 7.4 Hz), 2.73 (dq, 6H, J=14.8 Hz, 7.4 Hz), 2.78 (dq, 6H, J=14.8 Hz, 7.4 Hz), 6.89 (d, 6H, J=7.4 Hz), 6.92 (d, 6H, J=7.4 Hz), 7.06 (t, 6H, J=7.4 Hz); UV (cyclohexane) λ_{max} 210 nm (ε 2.0 x 10^5), 272 (4.7 x 10^4), 309 (shoulder); mass spectrum (field desorption) found m/z 1016. Irradiation of a solution of **2b** (7.7 mg) in 3-methylpentane (0.55 mL) in a sealed evacuated quartz tube utilizing a low-pressure mercury lamp (spiral, 125 W) provided a yellow, homogeneous solution that consisted predominantly of **1b** (>90% yield by ^1H NMR, see below). Cooling the photolysate to 0°C for 48 h provided as yellow crystals air- and moisture-sensitive pure digermene **1b**, mp 215-217°C, as evidenced from its spectral data: ^1H NMR (250 MHz, C_6D_{12}) δ 0.87 (t, 24H, J=7.5 Hz), 2.77 (q, 16H, J=7.5 Hz), 6.91 (d, 8H, J=7.5 Hz), 7.07 (t, 4H, J=7.5 Hz); UV (n-hexane) λ_{max} 263 nm (ε 1.3 x 10^4), 412 (8.4 x 10^3); mass spectrum (electron impact) found m/z 678.

Crystallographic Analysis of **1b**. The crystals are orthorhombic, *a*=9.735(1), *b*=19.027(3), *c*=19.293(3) Å, *U*=3574 $Å^3$, space-group *Pcnb*, *Z*=4, D_c=1.26 gcm^{-3}. In view of the air and moisture sensitivity of **1b**, a small single crystal was sealed under nitrogen in a Lindemann glass capillary tube. 1508 independent observed reflections $[|F_o| > 3\sigma(|F_o|), \theta \leq 55°]$ were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α radiation and using the ω-scan measuring routine. The structure, which is nearly isostructural with its silicon analog,[4] was solved by refining the silicon positions as germaniums and obtaining the positions of the aryl and ethyl carbons from a ΔF map. The structure was refined anisotropically with the phenyl rings being treated as idealized rigid bodies. Thermal motion in the structure is high and particularly pronounced in the ethyl groups. Refinement converged to give *R*=0.084, R_W=0.086.[a,b]

The structure (Figure 1) has a crystallographic two-fold axis bisecting the Ge=Ge bond. The geometry about the germanium atom is nearly the same as that observed in the corresponding disilene structure though with the C-Ge-C angle reduced. The C-Ge-C angle is 115.4(2)° and the C-Ge-Ge' angles are 118.7(1)° and 124.3(1)°, respectively [*cf* 117.6(2)°, 117.6(2)°, and 124.8(2)° for the equivalent angles in the silicon structure]. Unlike the silicon structure, the sum of these angles is not 360°, there being a slight pyramidal distortion at the germanium. The germanium is displaced 0.15 Å from the plane formed by the two aryl carbons and the other germanium atom. The Ge=Ge bond length is 2.213(2) Å and the Ge-C bonds are rotated with respect to each other about this bond. The two *cis* C-Ge-Ge'-C' torsion angles are -4° and 26° and the two *trans* torsion angles are -169° (Figure 2). These torsion angles can be interpreted as representing a twist angle (τ) of 11° about the Ge=Ge bond and an out-of-plane bending at the germanium atoms (χ_{Ge}) of 15°.[5] This result should be compared with the recently reported digermene structure (**3**)[3a] where more pronounced deviation from planarity at germanium is observed (χ_{Ge}=32°) and twisting about the Ge=Ge bond does not occur (τ=0°). It appears

(a) The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK. Any request should be accompanied by the full literature citation for this communication.

(b) Supplementary data available includes atomic co-ordinates, bond lengths and angles and temperature factors. See Announcement to Authors, *Tetrahedron Lett.*, 1983, **47**, 5154.

that twisting and out-of-plane bending of the substituents can be readily accomplished in the digermene system, in qualitative agreement with theoretical studies on the parent compound.[6] The Ge=Ge bond length of 1b (2.213 Å) is noticeably shorter than that of 3 (2.347 Å), and both of them in turn are shorter than the observed Ge-Ge bond lengths.[7]

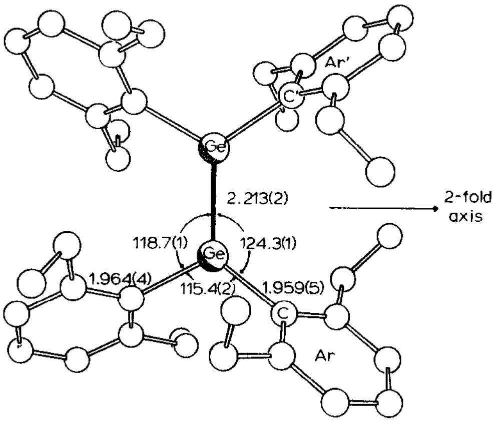


Fig. 1. Molecular structure of 1b.

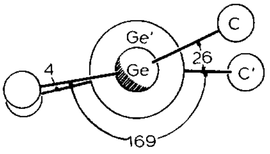
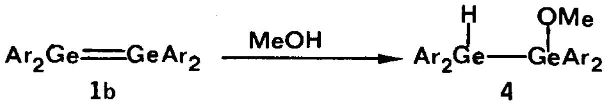


Fig. 2. Newman projection along the Ge=Ge' bond.

While recent theoretical investigations of digermene ($H_2Ge{=}GeH_2$) predict the more stable trans-bent conformer with $\tau=0°$ to have a χ_{Ge} value of 38.9°[6a] or 36.2°,[6b] the conformation of 1b is significantly influenced by the steric requirements of the 2,6-diethylphenyl substituents. The twisting of the Ge=Ge bond in 1b would in all likelihood minimize steric congestion. The small out-of-plane distortion at the germanium atoms probably reflects the increased stability of the pyramidal geometry relative to the analogous disilene[4] which is also consistent with recent theoretical calculations.[6,8]

The reaction of 1b with methanol reveals that this digermene retains its structural integrity in solution. Thus after photolytic preparation of 1b in 3-methylpentane, the solution was quenched by the addition of methanol and 1,1,2,2-tetrakis(2,6-diethylphenyl)-1-methoxydigermane (4) could be isolated in 56% yield (Eq. 2).[9] This result contrasts with the ethanolysis of 3 reported by Lappert and coworkers which provided bis[bis(trimethylsilyl)-methyl]germanium ethoxide (5, Eq. 3).[10] The latter compound arises from an insertion reaction of the corresponding singlet germylene that is present in solution.[3,10] It is evident that the structural integrity of the digermene species (i.e., dimeric vs monomeric) in solution is sensitive to substituent effects.



$$\underset{\mathbf{1b}}{Ar_2Ge{=}GeAr_2} \xrightarrow{MeOH} \underset{\mathbf{4}}{Ar_2\overset{H}{Ge}{-}\overset{OMe}{Ge}Ar_2} \qquad \text{Eq. 2}$$

Ar = 2,6-diethylphenyl

$$\underset{\mathbf{3}}{R_2Ge{=}GeR_2} \longrightarrow (2\ {:}GeR_2) \xrightarrow{EtOH} 2\ \underset{\mathbf{5}}{R_2Ge(H)OEt} \qquad \text{Eq. 3}$$

$R=CH(SiMe_3)_2$

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7. 2.543, 2,543, 2.537 Å in **2a** (ref. 2); 2.465 Å in $(Ph_2Ge)_4$ (L. Ross and M. Dräger, *J. Organomet. Chem.*, 1980, **199**, 195); 2.463, 2.457 Å in $(Ph_2Ge)_6$ (M. Dräger and L. Ross, *Z. Anorg. Allg. Chem.*, 1981, **476**, 95); 2.41 Å in H_6Ge_2 (E. G. Rochow and E. W. Abel, "The Chemistry of Germanium, Tin, and Lead," Pergamon, Oxford, 1975).

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9. Compound **3**: m.p. 167-170°; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.77 (t, 12H, J=7.4 Hz), 0.95 (t, 12H, J=7.4Hz), 2.32-2.76 (m, 16H), 3.40 (s, 3H), 5.62 (s, 1H), 6.94 (d, 4H, J=7.6 Hz), 6.96 (d, 4H, J=7.6 Hz), 7.18 (t, 2H, J=7.6 Hz), 7.19 (t, 2H, J=7.6 Hz); IR ($CHCl_3$) 3040 cm^{-1}, 2960, 2925, 2865, 2815, 2010 (ν_{GeH}), 1564, 1450, 1373, 1045 (ν_{GeOCH_3}).

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