where c is the polymer concentration (in grams per cubic centimeter), M_r is the molecular weight of the repeated unit, N is the Avogadro number; r is the diffusant radius calculated preferably from Eq. 2 with experimental data in the absence of polymer. Calculating r (Stokes-Einstein radius) in this way avoids several problems arising from solvent association (*21, 34*) and size (*18, 40*) and guarantees a consistent solution at least at vanishing polymer concentrations. When no experimental data are available, we recommend the radius estimation techniques described in (*15–17*). From Eq. 8, ϕ_{pr} is always larger than ϕ_p, for example, ranging from 4.7 times ϕ_p at low polystyrene concentrations to 3.8 times ϕ_p at 9% polystyrene.

Combining Eqs. 4 and 5 produces the equation

$$D_{eff} = \frac{kT}{6\pi\eta_0 r} \times \left(1 + \frac{d\ln\gamma_A}{d\ln x_A}\right) \times \left[\frac{2\eta_{pr}{}^* + \eta_0 - 2\phi_{pr}(\eta_{pr}{}^* - \eta_0)}{2\eta_{pr}{}^* + \eta_0 + \phi_{pr}(\eta_{pr}{}^* - \eta_0)}\right] \qquad (12)$$

where ϕ_{pr} is calculated from Eqs. 8 and 11; all of these terms are readily measured or estimated for most polymer solutions. Resulting values of D_{eff}, for $\eta_{pr}{}^* = \eta$ and $\eta_{pr}{}^* = \infty$, are plotted in Fig. 2B, where from solution density data

$$\phi_p = \frac{0.9975c}{0.818 + c} \qquad (13)$$

The agreement with experiment is far better than predictions from Eq. 2 or the Hiss-Cussler equation (*2*), and the constants are all estimated a priori in a way that is not yet possible with the equations of Ogston *et al.* (*26*) and Cukier *et al.* (*27*); we take this as evidence for the efficacy of Eq. 12 and presume further that some local viscosity relation of this type controls most polymer solution diffusion.

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Design of a Monomeric Arsinogallane and Chemical Conversion to Gallium Arsenide

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A monomeric arsinogallane containing a covalent gallium–arsenic bond has been prepared, and its molecular structure has been determined by x-ray crystallography. The compound reacted with *tert*-butanol at ambient temperature to yield the III-V semiconductor gallium arsenide as a finely divided amorphous solid. During the initial stages of the reaction small clusters of gallium arsenide were apparently present in solution. The band gaps of these particles, as observed by their absorption spectra, were larger than that of the bulk material. This work is a step toward the development of new molecular precursors for technologically important materials and the study of quantum size effects in small semiconductor particles.

GALLIUM ARSENIDE (GAAS) IS A III-V semiconductor, which compares favorably in certain respects (for example, carrier mobility and band gap) with silicon (*1*). Manufacture of devices based on this material depends on metal-organic chemical vapor deposition (MOCVD), a process involving reaction of trimethylgallium with an excess of the highly toxic gas arsine (AsH_3) at elevated temperatures (*2*). Many research groups are searching for alternative precursors and routes to GaAs. We report here the synthesis and characterization of the first monomeric arsinogallane, its chemical conversion into GaAs, and some observations on quantum size effects exhibited by very small particles of this semiconductor.

Addition of 2.0 equivalents of $Li(THF)_2$-$As(SiMe_3)_2$ (*3*) (THF = tetrahydrofuran, Me = methyl) to a pentane solution of $[(C_5Me_5)_2GaCl]_2$ (*4*) followed by filtration, evaporation of the solvent, and recrystallization of the product from pentane yielded yellow crystals of analytically pure arsinogallane $(C_5Me_5)_2Ga{-}As(SiMe_3)_2$ (**1** in Fig. 1) in 63% isolated yield (Scheme I) (*5*). The compound was very soluble in standard organic solvents and decomposed slowly when heated above 60°C or exposed to air. Cryoscopic determination of the molecular weight of **1** in benzene at two different concentrations gave molecular weights of 457 (0.19*m*) and 528 (0.10*m*), respectively,

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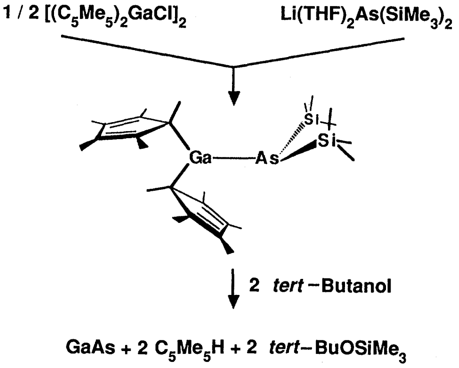
consistent with a monomeric structure (calculated molecular weight = 561) in solution. The room-temperature ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra featured equivalent pentamethylcyclopentadienyl rings and trimethylsilyl groups. However, after the sample was cooled in the probe of the spectrometer, the resonances of the C_5Me_5 rings broadened and finally split into two sets of resonances due to inequivalent rings. The trimethylsilyl groups remained equivalent. These observations are consistent with a monomeric structure in which a trigonal pyramidal As is covalently bound to a trigonal planar Ga such that the lone pair of the As atom lies in the mirror plane defined by the Ga and the atoms directly bound to it (see Scheme I). Rotation around the Ga–As single bond becomes fast enough at room temperature to lead to coalescence of the C_5Me_5 resonances (rotation rate $k_{\mathrm{rot}} = 27\ \mathrm{s}^{-1}$ at 215 K) (*6*). However, this model would leave no room for an expected donor-acceptor interaction between the As lone pair and the empty *p*-orbital on the three-coordinate Ga. To resolve this ambiguity we determined the crystal structure of **1** by x-ray diffraction (Fig. 1) (*7*). The compound is monomeric in the solid state too. A Newman projection down the As–Ga bond (see inset in Fig. 1) shows that the molecule indeed adopts the geometry described above, thus eliminating any possibility of As–Ga π-bonding. This particular arrangement, which is very likely the result of severe steric interactions between the bulky substituents, may also be the reason for the unprecedented monomeric nature of **1**. Head-to-tail dimerization of two arsinogallanes by means of Lewis acid-base interactions would require coplanarity of the donor and acceptor orbitals in each molecule. Comparison with other structurally characterized arsinogallanes (*8*) reveals that **1** exhibits a rather short Ga–As bond. At 2.433(4) Å (where the number in parentheses is the uncertainty in the last decimal place) it is just short of the sum of the covalent radii of the two elements (2.46 Å) (*9*).



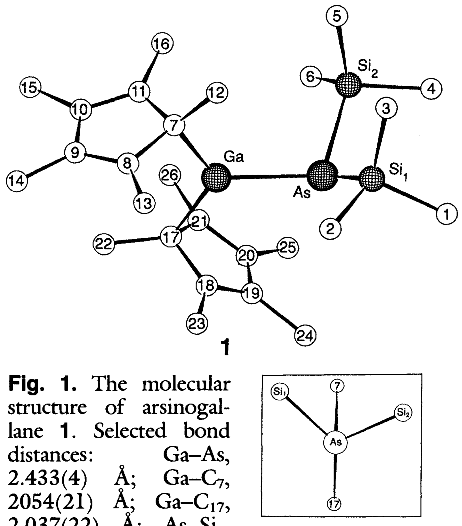
Scheme 1

The design of **1** had included a provision for the ultimate removal of all substituents on the binuclear core of the molecule. In this scenario, the basicity of the Ga-bound carbon was to be used to introduce another substituent, which would in turn form a strong bond to silicon, thus driving the formal reduction to GaAs. Accordingly, reaction of **1** with *tert*-butanol in pentane yielded 2 equivalents each of pentamethylcyclopentadiene and *tert*-butyl(trimethylsilyl) ether. The only other product was a reddish powder, which precipitated from the reaction solution. Elemental analysis and scanning electron microprobe analysis of this powder showed it to be GaAs with some organic impurities. The x-ray powder diffraction pattern of the material exhibited only two very broad features centered around the strongest lines expected for GaAs. However, after the amorphous material had been annealed at 500°C for 48 hours, the sample exhibited the diffraction pattern of crystalline GaAs (*10*).

Kinetic measurements belied the apparent simplicity of this reaction. Rate constants proved irreproducible from run to run, seemingly dependent on the history of the batch of **1** used in the experiments. On the basis of several lines of evidence, we now believe that the decomposition of **1** is actually catalyzed by a small amount of a chloride-containing impurity, probably $[(C_5Me_5)(Cl)Ga\text{–}As(SiMe_3)_2]_n$. Reaction of the alcohol with this molecule may liberate HCl, which apparently facilitates the decomposition reaction in an as yet undetermined way.

Regardless of the exact mechanism, it seemed entirely possible that the primary product of the above reaction was monomeric GaAs. In a secondary process these molecules then presumably combined to form dimers, clusters, microscopic particles, and finally macroscopic objects (albeit as a finely divided powder). The study of so-called quantum size effects, exhibited by very small particles of semiconductors or metals, is an area of growing interest (*11*). This interest is fueled not only by fundamental curiosity but also by the need to understand the properties of existing devices that exhibit structure on a near atomic scale.

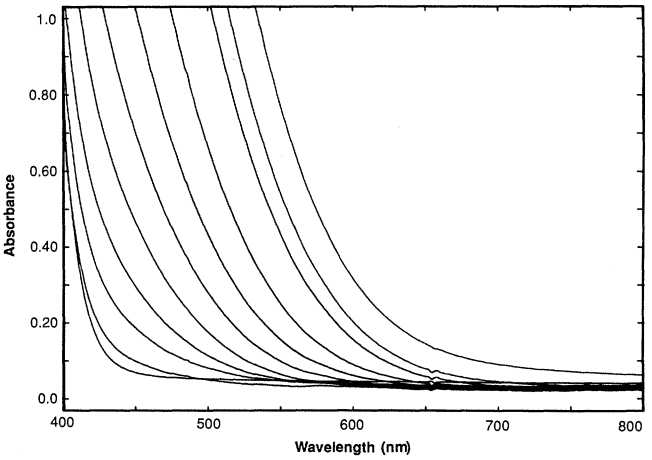
It has been shown that the absorption spectra of semiconductors change with particle size (*11*). As the discrete energy levels of single molecules merge into the bands of the extended solid, the absorption edge of the material is red-shifted until it finally reaches the band gap of the bulk. Depending on the particular material, this point is typically reached with particle diameters on the order of several hundred angstroms. Figure 2 depicts a series of absorption spectra taken after addition of an excess of *tert*-butanol to a THF solution of **1**. Solutions of the arsinogallane were faintly yellow because of an absorption maximum at 246 nm. Addition of the alcohol caused the solution to change color from yellow through orange to red-brown. This change took place dur-



1

Fig. 1. The molecular structure of arsinogallane **1**. Selected bond distances: Ga–As, 2.433(4) Å; Ga–C_7, 2054(21) Å; Ga–C_{17}, 2.037(22) Å; As–Si_1, 2.355(8) Å; Ga–Si_2, 2.328(8) Å; interatomic angles: C_7–Ga–As, 124.0(6)°; Ga–As–Si_1, 108.0(2)°; Si_1–As–Si_2, 103.7(3)°

Fig. 2. Absorption spectra of a THF solution of **1** at various times after the addition of 17 equivalents of *tert*-butanol. From left to right, the elapsed time intervals for the spectra are 0, 8, 15, 23, 33, 45, 60, 80, 120, 166, and 853 min.



ing several hours, and the solution appeared perfectly homogeneous at all times. The spectra showed a continuous red shift of the onset of absorption with time. Presumably 1 decomposed and formed monomeric GaAs, which was solvated by the donor THF. In a subsequent association, these monomers aggregated to GaAs clusters of increasing size. Brus has calculated the size dependence of the energy of the lowest excited state for clusters of various semiconductors, including GaAs (*12*). According to these calculations (for an absorption onset of about 600 nm for the rightmost curve in Fig. 2), the average particle size in the solution at that time was estimated as 60 Å.

As our understanding of the chemistry of mixed-metal main-group organometallics develops, chemists will be able to design a new generation of precursors for III-V semiconductors. In addition, the study of these molecules is already revealing an intriguing diversity of reaction pathways and has provided an opportunity to investigate the physical properties of small clusters of these solids.

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Congenital Poisoning by Polychlorinated Biphenyls and Their Contaminants in Taiwan

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In 1979, a mass poisoning occurred in Taiwan from cooking oil contaminated by thermally degraded polychlorinated biphenyls. Because these chemicals persist in human tissue, children born to female patients after the outbreak were exposed in utero. In 1985, 117 children born to affected women and 108 unexposed controls were examined and evaluated. The exposed children were shorter and lighter than controls; they had abnormalities of gingiva, skin, nails, teeth, and lungs more frequently than did controls. The exposed children showed delay of developmental milestones, deficits on formal developmental testing, and abnormalities on behavioral assessment. These findings are most consistent with a generalized disorder of ectodermal tissue. This syndrome is one of very few documented to result from transplacental exposure to pollutant chemicals.

COOKING OIL CONTAMINATED BY polychlorinated biphenyls (PCBs) and dibenzofurans led to an outbreak of illness (called *yucheng* or "oil disease") in Taiwan. The illness consisted of chloracne, hyperpigmentation, and meibomian gland dilatation among other findings (*1, 2*). The epidemic was noted in May 1979, and the oil was removed from the market in October; cases were identified retrospectively from as far back as December 1978. There is a registry of about 2000 persons who were exposed to the oil. A similar outbreak ("*yusho*") had occurred in Japan in 1968.

Because these chemicals persist in human tissue [similar dioxins have half-lives in humans of about 7 years (*3*)], offspring of female patients continue to be born affected, even though maternal exposure has ceased. By 1983, 8 of 39 hyperpigmented children born to exposed mothers had died (*1*). In April 1985 we performed a field survey of all living children who were known to have been in utero during or after the period of oil contamination. These children would have had transplacental exposure and possibly exposure through breast milk, but would not themselves have consumed the contaminated oil.

Seventy-four women in the health department's registry had living children born between June 1978 and March 1985. Use of these dates should identify any child with transplacental exposure, since the latent period during which oil was consumed but mothers were asymptomatic was about 6 months. Chinese-speaking nurses interviewed the mothers in their homes and scheduled the examinations. The women reported 159 pregnancies in this time; 3 were ongoing, 5 miscarried, 8 were aborted, 6 were stillborn, and 5 born live later died, leaving 132 living children. We obtained usable information on 128. One more child died between interview and examination. Twenty-nine families had 1 eligible child, 34 had 2, 9 had 3, and 2 had 4. Controls came from 96 families who lived in the same neighborhoods. These 96 mothers reported 205 pregnancies in this period; 3 were ongoing, 8 miscarried, 4 were aborted, and 190 produced live births; we obtained data on 115. The exposed children averaged 32 months old, range from 1 to 82 months; the controls averaged 31 months, range 3 to 98

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