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Free Rotation of Methyl Groups in Dimethyltin Difluoride[1a]

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The structure of dimethyltin difluoride, $(CH_3)_2SnF_2$, has recently been determined by X-ray diffraction[2] to be tetragonal, with $a = 4.24$ and $c = 14.16$ A and two "molecules" per unit cell. The crystal arrangement consists of an infinite two-dimensional network of tin atoms and bridging fluorine atoms, with the methyl groups above and below the plane, completing octahedral coordination of the tin. The structural data, however, yielded little information on the methyl-group hydrogen atoms, owing to the small contribution of the hydrogen to the X-ray scattering. Since the methyl groups lie on a fourfold symmetry axis, it is reasonable to assume that they are either rotating or at least fourfold disordered.

In this note we report a study of the rotation of the methyl groups in $(CH_3)_2SnF_2$ by total cross-section measurements with subthermal neutrons. The neutron cross-section method has been shown to be quite useful for the investigation of the motions of hydrogen atoms in solids and liquids.[3-6] At "cold" neutron energies ($E_n \ll 0.025$ ev) the total scattering cross section, σ_s, has the form σ_s (barns) $= a + c\lambda_n$, where λ_n is the neutron wavelength (A). The slope c (barns/A) is a direct measure of the change in the inelastic scattering with wavelength and basically depends on the population of excited rotational and vibrational states available for exchange of energy with the cold neutrons incident on the scattering sample. Owing to the large, incoherent proton-scattering cross section, the slopes for hydrogenous compounds will primarily be a measure of the freedom of motion of the hydrogen atoms.

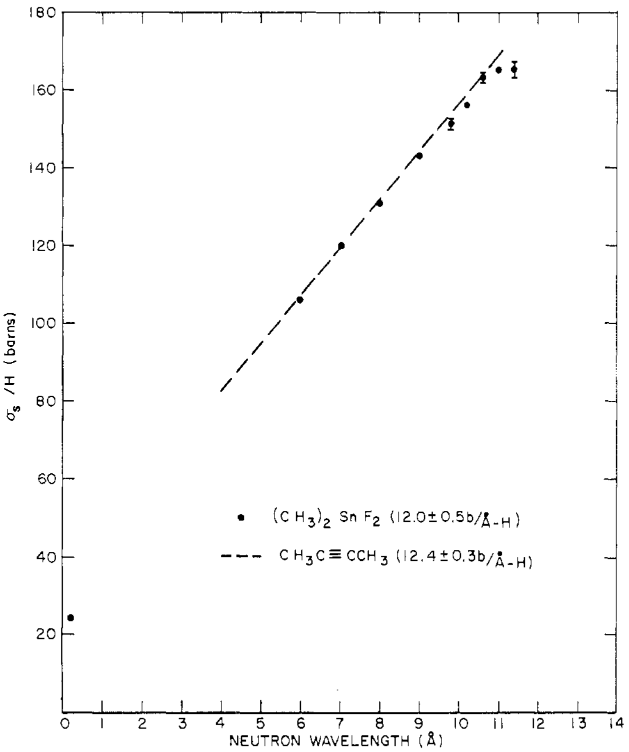

Figure 1.—Neutron-scattering cross sections per hydrogen atom for $(CH_3)_2SnF_2$ at 23°. Previous cross-section results for $CH_3C{\equiv}CCH_3$ are also shown (dashed line). The error bars represent the statistical errors due to counting ($\lesssim 1\%$). The errors on the slopes include statistical errors, as well as the estimated systematic uncertainties due to sample-packing and Bragg-scattering effects.

The total cross sections for polycrystalline, reagent grade $(CH_3)_2SnF_2$ were obtained by neutron transmission measurements, using the Columbia crystal spectrometer at the Brookhaven graphite reactor.[7] The technique of sample preparation has been described elsewhere.[4-6] Cross sections per molecule were corrected for neutron absorption and divided by the number of hydrogen atoms to obtain cross sections per hydrogen atom (σ_s/H). The results are plotted in Figure 1. Also shown in the figure are cross-section results previously measured for dimethylacetylene[5] (dashed line), a compound for which the barrier to rotation of the methyl groups is considered to be negligible.[8] The scatter of the points above 10 A in the $(CH_3)_2SnF_2$ results probably arises from intense Bragg scattering of the long-wavelength neutrons.

The cross-section slope for $(CH_3)_2SnF_2$ is 12 barns/A H, with an estimated error of ±0.5, quite close to the value of 12.0 ± 0.4 for $CH_3C{\equiv}CCH_3$. The similarity of these results is evidence for a low barrier to rotation in $(CH_3)_2SnF_2$, with only slight interaction of the methyl groups with other methyl groups and atoms in the crystal lattice. It is interesting to note that the C–Sn–C distance (4.2 A)[2] is also very close to the distance between methyl groups in $CH_3C{\equiv}CCH_3$ (4.3 A).

The slope of 12 is also quite similar to those measured for nonadjacent methyl groups in methylbenzenes

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[1] (a) This work supported in part by the U. S. Atomic Energy Commission; (b) National Bureau of Standards; (c) Brookhaven National Laboratory.

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(11.4 barns/A H), which also possess a very low rotational barrier.[4,8] Moreover, recent theoretical calculations indicate that the cross-section slope for a methyl group freely rotating in one dimension is about 12,[9] again in agreement with the present results. The total cross-section technique is sensitive over a range of rotational barriers. For example, the slope for a methyl-group barrier of 1 kcal/mole is about 9 barns/A H.[4,6,9] From these comparisons, it appears certain that the methyl groups in $(CH_3)_2SnF_2$ are essentially freely rotating, with a barrier to rotation less than a few tenths of 1 kcal.

It would be interesting to extend these measurements to compounds with other than octahedral coordination, as well as to similar trimethyl compounds in which the methyl-group barrier might be considerably greater.

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(9) P. S. Leung, J. J. Rush, and T. I. Taylor, unpublished work.

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Reactions of Phosphonitrilic Chloride with *p*-Nitrophenol

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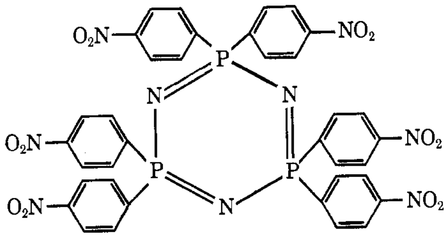
As reported by Brown,[1] attempts to synthesize nitrophenoxy-substituted phosphonitrilic chlorides by the reaction of trimeric phosphonitrilic chloride with sodium nitrophenoxides, prepared from nitrophenols and sodium, in a molar ratio of approximately 1:3 in boiling toluene failed to give any defined compound.



I

In search for hexakis(*p*-nitrophenoxy)phosphonitrile (I) we investigated the reaction of trimeric phosphonitrilic chloride with sodium *p*-nitrophenoxide in a 1:6 molar ratio. As did Brown, we obtained a dark brown, resinous reaction product from which small amounts of 2-chloro-2,4,4,6,6-pentakis(*p*-nitrophenoxy)-phosphonitrile (II) and 2,4,6-trichloro-2,4,6-tris(*p*-nitrophenoxy)phosphonitrile (III) were isolated after several extractions and recrystallizations. Structure III is supported by nuclear magnetic resonance spectroscopy. The proton-irradiated ^{31}P spectrum shows only one singlet at 17.4 ppm and, hence, indicates three equivalent phosphorus atoms. All efforts to isolate—besides II and III—the other yet unknown chloro(*p*-nitrophenoxy)phosphonitriles as well as compound I were futile. Attempts to synthesize tetrachlorobis(*p*-nitrophenoxy)phosphonitrile (IV) from 1 mole of $(PNCl_2)_3$ and 2 moles each of the phenol and triethylamine in refluxing toluene did not result in IV, but in substantial quantities of pure 2,4,4,6,6-pentachloro-2-(*p*-nitrophenoxy)phosphonitrile (V). Also isolated was a trace quantity of octakis(*p*-nitrophenoxy)-phosphonitrile (VI). Its formation was traced back to a small amount of $(PNCl_2)_4$ present in the starting material. The isolation of VI was facilitated by its low solubility in toluene and ether. Whereas the reaction of trimeric phosphonitrilic chloride with sodium *p*-nitrophenoxide had not afforded any amount of I, the corresponding reaction with the tetramer gave VI in 79% yield. Eventually, the trimeric compound I was obtained in 87% yield by reaction of $(PNCl_2)_3$ with excessive amounts of *p*-nitrophenol and potassium hydroxide in boiling xylene. Surprisingly, the melting point of 263–264°, recorded for the product obtained by this procedure, does not correspond with that of 212–214° found by Yokoyama,[2] who reported the preparation of I from $(PNCl_2)_3$ and sodium *p*-nitrophenoxide in undisclosed but apparently low yield.

Experimental Section

Melting points were determined in a modified Thiele Apparatus and are not corrected. The ^{31}P spectrum was obtained at 19.3 MHz with a Varian HR Type nmr spectrometer. Irradiation of H was done with an NMR Specialties HD-60 spin decoupler. The chemical shift was measured by the side-band technique relative to external 85% phosphoric acid. Melting points and results of the elemental analyses are compiled in Table I.

2,2,4,4,6,6-Hexakis(*p*-nitrophenoxy)phosphonitrile (I).—A mixture consisting of 209 g (1.5 moles) of *p*-nitrophenol, 94 g of potassium hydroxide, and 1000 ml of xylene was slowly heated with stirring to 80°. At this temperature, 70 g (0.2 mole) of $(PNCl_2)_3$ dissolved in 250 ml of xylene was added dropwise over a period of 1 hr. The mixture was then refluxed until 35 ml of water had collected in a Stark and Dean distilling trap (*ca.* 28 hr). The yellow precipitate was separated and washed with warm 10% aqueous potassium hydroxide and finally with water. Recrystallization of the dried solid from dimethylformamide and thereafter from cyclohexanone afforded 166 g of pure I.

2,2,4,4,6,6,8,8-Octakis(*p*-nitrophenoxy)phosphonitrile (VI).—To a stirred suspension of 36 g (1.5 moles) of sodium hydride in 250 ml of ether was added a solution of 209 g (1.5 moles) of *p*-nitrophenol in 350 ml of ether at such a rate that gentle refluxing resulted. The ether solvent was then replaced by 800 ml of xylene, and a solution of 70 g (0.15 mole) of $(PNCl_2)_4$ in 400 ml of xylene was added. After refluxing for 27 hr, the mixture was worked up as described for I. Recrystallization from dimethylformamide rendered 152 g of pure VI.

2,4,4,6,6-Pentachloro-2-(*p*-nitrophenoxy)phosphonitrile (V).—Solutions of 139.1 g (1 mole) of *p*-nitrophenol in 500 ml of toluene and 101.2 g (1 mole) of triethylamine in 500 ml of toluene were added dropwise and simultaneously to a boiling mixture of 173.8

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