H, 3.41. Found: C, 56.04; H, 3.55.

Supplementary Material Available: ^{1}H and/or ^{13}C NMR spectra of 2-4 and 6-8 (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Solubility of C_{60} in Organic Solvents

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A large number of reports have appeared in the literature in the last couple of years on the preparation, properties, and reactions of C_{60} (Buckminsterfullerene).[1-7] The solubility of C_{60} in organic solvents plays a crucial role in its extraction, chromatographic separation, and reactions in solvent media. In fact, the poor solubility of C_{60} in most organic solvents has been one of the main impediments to studying the properties of C_{60}. However, there has been no systematic investigation of the solubility of C_{60} in different solvents, though qualitative observations have been made on the solubility behavior. Ajie et al.[8] reported that the solubility of a mixture of C_{60} and C_{70} in benzene was "about 5 mg/mL" at 25 °C. They also mentioned that the compound dissolved with difficulty in chloroform, dichloromethane, tetrachloromethane, diethyl ether, etc. In a recent report on the preparative separation of C_{60} and C_{70}, Meier and Selegue[9] employed toluene solutions saturated with fullerenes, and they reported a concentration of ca. 6-8 mg/mL. In this paper, we report the solubility of pure C_{60} in various organic solvents and note that the solubility shows a correlation with the solubility parameter of the solvent.

Table I. Solubility of C_{60} in Organic Solvents (at 303 K)

solvent	solubility parameter[a] $(J/cm^3)^{1/2}$	solubility (μg/mL)
isooctane	14.17	26
pentane	14.52	4
hexane	14.85	40
octane	15.45	25
decane	15.81	70
dodecane	16.07	91
tetradecane	16.24	126
cyclohexane	16.77	51
carbon tetrachloride	17.59	447
mesitylene	18.04	997
toluene	18.20	2150
benzene	18.82	1440
methylene chloride	20.04	254
dioxane	20.50	41
carbon disulfide	20.50	5160

[a] Refers to the value at 25 °C.

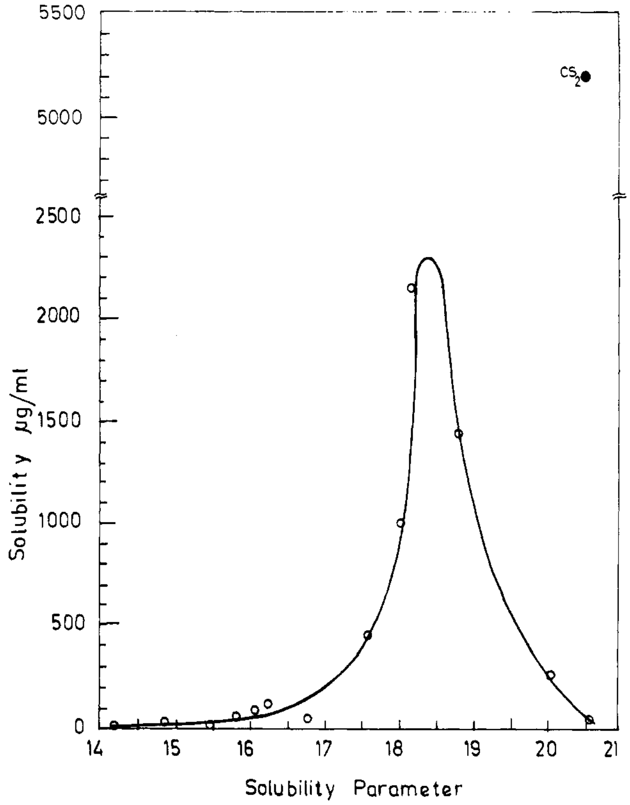

Figure 1. Variation of the solubility of C_{60} in different solvents as a function of the solvent solubility parameter (δ).

The solubility of C_{60} in organic solvents at 303 K as measured in our work is given in Table I. The values given are averages of duplicate measurements. The solubility is rather low; in fact, even in aromatic solvents the solubility is comparable to that of inert gases. For example, the solubility of C_{60} in benzene is 1.44 mg/mL, which corresponds to a mole fraction of 1.78×10^{-4}. The solubility of C_{60} in benzene may be compared to the reported solubility of neon in benzene (mole fraction 1.07×10^{-4} at 298 K for a pressure of 1 atm).[10] C_{60} has been described as a van der Waals solid, similar to the solid form of inert gases, with little interaction between the molecules. The solubility of C_{60} can thus be expected to be generally low because the energy required for the breaking of a large number of solvent bonds during the dissolution is not adequately compensated for by the interaction between the solute and the solvent. The higher solubility of C_{60} in aromatic solvents as compared to aliphatic solvents can be explained on the basis of a better interaction between the solute and the solvent molecules in the former case.

It is interesting to note that the solubility of C_{60} in aliphatic hydrocarbons increases with the carbon number of the solvent. This can be explained in terms of Hildebrand's theory of regular solutions,[10] in which the solubility

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(1) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* 1990, *347*, 354.

(2) Iqbal, Z.; Baughman, R. H.; Ramakrishna, B. L.; Khare, S.; Murthy, N. S.; Bornemann, H. J.; Morris, D. E. *Science* 1991, *254*, 826.

(3) Zhu, Q.; Zhou, O.; Coustel, N.; Vaughan, G. B. M.; McCauley, J. P., Jr.; Romanov, W. J.; Fischer, J. E.; Smith, A. B., III. *Science* 1991, *254*, 545.

(4) Olah, G. A.; Bucsi, I.; Lambert, C.; Aaniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Surya Prakash, G. K. *J. Am. Chem. Soc.* 1991, *113*, 9385.

(5) Greaney, M. A.; Gorun, S. M. *J. Phys. Chem.* 1991, *95*, 7142.

(6) Mathews, C. K.; Vasudeva Rao, P. R.; Srinivasan, T. G.; Ganesan, V.; Sivaraman, N.; Lakshmi Narasimhan, T. S.; Kaliappan, I.; Chandran, K.; Dhamodaran, R. *Curr. Sci.* 1991, *61*, 834.

(7) Allemand, P. M.; Koch, A.; Wudl, F.; Rubin, Y.; Diedrich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* 1991, *113*, 1050.

(8) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diedrich, F.; Fostiropoulos, K.; Huffman, D. R.; Kratschmer, W.; Yves, R.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* 1990, *94*, 8630.

(9) Meier, M. S.; Selegue, J. P. *J. Org. Chem.* 1992, *57*, 1924.

(10) Hildebrand, J. H.; Prausnitz, J. J.; Scott, J. L. *Regular and Related Solutions*; Van Nostrand Reinhold Co.: New York, 1970.

0022-3263/92/1957-6077$03.00/0

is correlated with the solubility parameter of both the solvent and the solute. The solubility parameter is defined as

$$\delta = [(\Delta H - RT)/V]^{1/2}$$

where ΔH is the heat of vaporization, T, the temperature, and V, the molar volume.

In Figure 1, the solubility of C_{60} is plotted as function of the solubility parameter of the solvent. The solubility first increases to a maximum at a solubility parameter value of ca. 18.5 and then decreases. Theory predicts such behavior, with the solubility exhibiting a maximum when the solubility parameter of the solvent matches that of the solute. (In fact, the measurement of solubility in various solvents is one of the procedures used to estimate the solubility parameter of solutes.)[11] A similar trend has been observed, for example, in the solubility of xenon in various solvents.[12] Thus, Figure 1 suggests that the solubility parameter of C_{60} is ca. 18.5. The data for a few hydrocarbons with low carbon numbers seem to deviate from the trend, but the deviation is understandable because the presence of even very small concentrations of aromatic impurities might significantly influence the measured solubility at these levels.

It is not possible to compare our solubility data with the data available in the literature because the data reported by earlier authors (Ajie et al.;[8] Selegue et al.[9]) are qualitative in nature, and they refer to mixtures of C_{60} and C_{70}, not to C_{60} alone.

We can attempt to roughly estimate the solubility parameter of C_{60} from the available data on the heat of sublimation. The heat of sublimation of C_{60} was recently measured in our laboratory by Knudsen cell mass spectrometry[13] in the temperature range 600–800 K. A value of 181.4 kJ/mol was reported for this temperature range; the value of the heat of sublimation at 303 K is expected to be slightly higher, depending on the heat capacity of the vapor and solid phases. The difference is expected to be on the order of 10–20 kJ/mol. The heat of vaporization of liquid C_{60} can be calculated by subtracting the heat of fusion of the compound from the heat of sublimation. Considering the nature of the C_{60} molecule and the data available on the heat of fusion of aromatic compounds such as phenanthrene, biphenyl, etc., we can estimate the value of heat of fusion of C_{60} to be on the order of 20–30 kJ/mol. Thus, the heat of vaporization of liquid C_{60} at 303 K can be estimated to be less than the heat of sublimation by about 10%. Since no data are available on the molar volume of liquid C_{60}, we assumed it to be approximately equal to the molar volume of C_{60} solid (429 cm^3/mol) calculated from its density (1.678 g/cm^3). Thus, the solubility parameter of C_{60} at 303 K is estimated, from its heat of vaporization and molar volume, to be 19.35. The value obtained from such a computation will necessarily be approximate in view of the assumptions involved. In spite of the limitations of this computation, the solubility parameter estimated from the solubility data shown in Figure 1 is in reasonable agreement with that calculated from the heat of vaporization.

An important exception to the correlation of solubility with the solubility parameter is carbon disulfide. The solubility of C_{60} in this solvent is by far the highest measured in any solvent and is orders of magnitude higher than what could be expected based on the solubility parameter. In contrast, the solubility in dioxane, which has the same solubility parameter as carbon disulfide, agrees with the trend. It is difficult to explain why carbon disulfide, which is a "normal" nonpolar liquid, stands out as an exception, while solvents such as dioxane and dichloromethane show the expected level of solubility. We have not observed any significant change in the UV absorption spectrum of C_{60} in hexane in the presence of a 500-fold molar excess of carbon disulfide. However, the typical concentrations of C_{60} and carbon disulfide in these experiments were in the range of 10^{-5} and 5×10^{-3} M, respectively. Recording of the absorption spectrum of C_{60} in pure carbon disulfide alone was not useful, since carbon disulfide itself strongly absorbs in the region of interest (328 nm). Thus, it is difficult to reach any conclusion regarding chemical interactions between C_{60} and carbon disulfide from our spectrophotometric observations. Further studies are needed to find a suitable explanation for the high solubility of C_{60} in carbon disulfide.

As mentioned before, the development of techniques for the isolation of C_{60} and C_{70} is hampered by the poor solubility of fullerenes in most organic solvents. In the conventional technique used for the isolation of the fullerenes, C_{60} is eluted from a neutral alumina column with hexane (or hexane–5% toluene). C_{70} is subsequently eluted with a hexane–20% toluene mixture. This isolation procedure requires additional steps for the separation of hexane and toluene by distillation after recovery of the fullerenes, if the solvents are to be reused. In addition, the technique requires large volumes of hexane, and considerable tailing is observed in the elution of C_{60}. The solubility data obtained in the present work indicate that aliphatic solvents with higher carbon numbers might be more suitable than hexane for use in the chromatographic separation of fullerenes in view of the higher solubility of C_{60} in these solvents. Indeed, we have been able to obtain clear separation of C_{60} and C_{70}, as well as complete elution from alumina, using the single solvent system of dodecane. However, the use of dodecane was found to have one disadvantage: the high boiling point of dodecane necessitated the use of vacuum during the recovery of the solvent from the eluted solution.

Using cyclohexane as the solvent, we have been able to obtain very good separation and complete recovery of the fullerenes on alumina. In a typical experiment, 100 mg of fullerene mixture was loaded on an alumina column of 60-mm diameter and 480-mm height. After elution, the absorption spectrum of the eluate was measured. Both C_{60} and C_{70} could be completely separated and recovered with only 3–4 L of solvent, since the solvent from the eluate could be repeatedly used after distillation. It is possible that the use of aliphatic hydrocarbons with carbon numbers between 7 and 9 will also provide the advantages of single solvent recovery.

Experimental Section

Preparation of Fullerenes. Graphite soot, obtained by passing an ac discharge between spectroscopic grade graphite electrodes in a helium atmosphere of 100–200 Torr, was subjected to toluene soxhlet extraction to recover the fullerenes. Details of the techniques used are described elsewhere.[6] The C_{60} used in the solubility experiments was obtained by chromatographic separation. HPLC-grade or AR-grade solvents were employed for the solubility measurements. Whenever necessary, aliphatic solvents were purified of aromatic impurities, by chromatography.

Solubility Measurements. The procedure for measurement of solubility consisted of adding an excess of C_{60} solid to the solvent under study in an equilibration tube that was maintained at a constant temperature of 303 ± 0.1 K in a water bath. The contents

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[11] Barton, A. F. M.; *Handbook of Solubility Parameters and other Cohesion Parameters*, 2nd ed.; CRC Press: Boca Raton, FL, 1991; p 354.

[12] Steinberg, M.; Manowitz, B. *Ind. Eng. Chem.* **1959**, *51*, 49.

[13] Mathews, C. K.; Sai Baba, M.; Lakshmi Narasimhan, T. S.; Balasubramanian, R.; Sivaraman, N.; Srinivasan, T. G.; Vasudeva Rao, P. R. *J. Phys. Chem.* **1992**, *96*, 3566.

of the glass equilibration tube were stirred for a period of 5 h, as initial studies had established that equilibrium was reached within about 2 h. The tube was then centrifuged, a sample (usually 100–200 μL) of the solution phase was withdrawn, and the absorption spectrum was measured after the sample was diluted with spectroscopic grade *n*-hexane. Absorbance measurements were carried out with a Shimdazu UV-2100 spectrophotometer. The solubility of C_{60} was calculated from the absorbance value at 328 nm. The validity of the Beer–Lambert law was checked by measuring the absorbance of standard solutions of C_{60} in hexane. The extinction coefficient at 328 nm was found to the 51238 $L{\cdot}mol^{-1}{\cdot}cm^{-1}$, in agreement with the reported value of 51290 $L{\cdot}mol{\cdot}cm^{-1}$.[7]

Chromatographic Separation Experiments. For the separation experiments, an alumina column of 60-mm diameter and 480-mm length was used. A benzene solution of the fullerene mixture was loaded onto alumina in a rotary evaporator. The loaded alumina was transferred to the column, and the fullerenes were eluted with cyclohexane. In some experiments, the fullerene mixture was dissolved in cyclohexane, before being loaded onto the column. The separation achieved in both methods was satisfactory.

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Synthesis of Amino-Containing Phosphines. The Use of Iminophosphorane as a Protecting Group for Primary Amines

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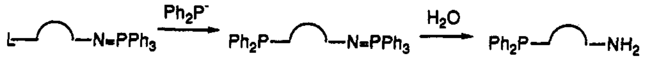
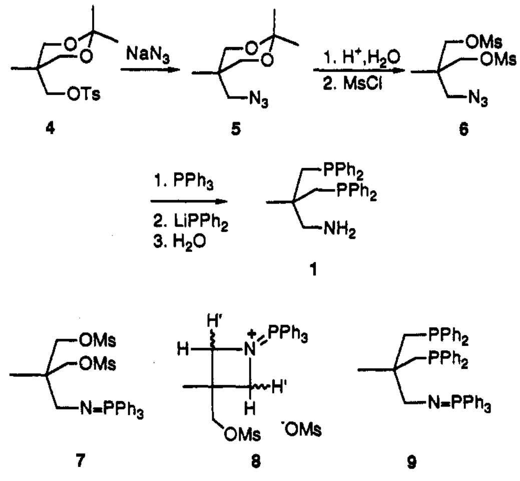
In the design of polydentate phosphines, the incorporation of "mixed" donor atoms for better control over the reactivities of the metal ions has received much attention recently. In this arena the copresence of primary amine and phosphine groups in the same ligand is of particular interest. However, the synthesis of these amino-containing phosphines has proven a challenge to chemists. In this report we describe the synthesis of ligands bearing both primary amine and tertiary phosphine donors.

Tertiary phosphines are readily prepared by the nucleophilic displacement of alkyl halides and sulfonates with R_2P^- anions; the amino group ultimately required, however, cannot be present in the substrate due to the possibility of N-alkylation. While there are many suitable protecting groups available,[1] the lengthy reaction sequence which this route would entail is not appealing. It would be ideal, however, if a simple derivative of the amine could be generated in the synthetic step. At the very least, one step could be deleted from the process. In order for this method to be effective, it is critical that the amino derivative be stable with respect to the phosphide anion and that it degrade readily to the free amine. It occurred to us that an excellent condidate for this role might be iminophosphorane, given that its hydrolytic cleavage behavior is well documented.[2-4] To explore this idea (Scheme I), we investigated the synthesis of amino-containing phosphines **1**–**3**.

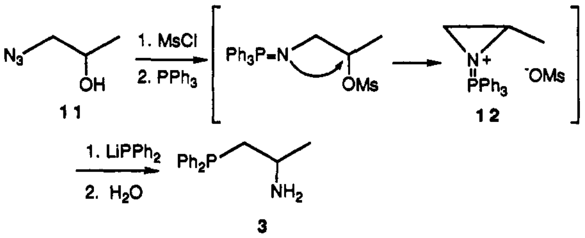
Scheme I



Scheme II



Scheme III



The synthesis of **1** is shown in Scheme II. Nucleophilic substitution of **4**[5] by sodium azide in DMF provided **5**. Hydrolysis of **5** in a mixture of THF and water under acidic conditions gave the corresponding diol, which was subsequently converted into mesylate **6** by treatment with mesyl chloride in the presence of triethylamine. Conversion of **6** to aminophosphine **1** was accomplished in a one-pot reaction by the following sequence: (i) formation of iminophosphorane **7** using triphenylphosphine in THF solution, (ii) substitution reaction by lithium diphenylphosphide, (iii) removal of the iminophosphorane protecting group. The desired tripodal phosphine **1** was isolated as a viscous oil (51% yield) by chromatography. The stability of iminophosphorane toward phosphide is evidenced by the formation of species **9**, which was characterized by its spectral data (see Experimental Section).

In analogy to **1**, this process has been successfully applied to the preparation of (3-aminopropyl)diphenylphosphine (**2**)[6] and (2-aminopropyl)diphenylphosphine (**3**) from the corresponding azides 1-azido-3-chloropropane (**10**) and 1-azido-2-propanol (**11**), respectively. The selective formation of **3** can be rationalized by the intervention of aziridine **12**[7] via nucleophilic attack of iminophosphorane at the adjacent carbon (Scheme III) and a subsequent ring

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(1) Greene, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Synthesis*, 2nd ed.; John Wiley Interscience: New York, 1991.

(2) For a review of iminophosphorane, see: Gololobov, Y. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437.

(3) Hassner, A.; Galle, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 3733.

(4) (a) Briggs, E. M.; Brown, G. W.; Jiricny, J.; Meidine, M. F. *Synthesis* **1980**, 295. (b) Zimmer, H.; Jayawant, M.; Gutsch, P. *J. Org. Chem.* **1970**, *35*, 2826. (c) Vaultier, M.; Knouzi, N.; Carrie, R. *Tetrahedron Lett.* **1983**, *24*, 763. (d) Bachi, M. D.; Vaya, J. *J. Org. Chem.* **1979**, *44*, 4393. (e) Zimmer, H.; Singh, G. *J. Org. Chem.* **1963**, *28*, 483. (f) Ittah, Y.; Sasson, Y.; Shahak, I.; Tsaroom, S.; Blum, J. *J. Org. Chem.* **1978**, *43*, 4271.

(5) Gash, V. W. *J. Org. Chem.* **1972**, *37*, 2197.

(6) DuBois, D. L. *Inorg. Chem.* **1984**, *23*, 2047.

(7) The formation of **12** was reported in the reaction of 2-iodopropyl azide with Ph_3P; see ref 3.

0022-3263/92/1957-6079$03.00/0