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13. ABSTRACT *(Maximum 200 words)*

Described are several solvents for the dissolution of fullerenes. The two best solvents found were 1,2-dichlorobenzene and 1-methylnaphthalene which dissolve C_{60} up to 24.6 and 33.2 mg mL^{-1}, respectively. The solubility data was obtained gravimetrically. Precipitates were obtained when C_{60} was treated with 1,3,5-trimethylbenzene or 1,2,4-trichlorobenzene. Scanning electron micrographs and thermogravimetric analysis data were obtained on the precipitates and compared to the data obtained for pure C_{60}. The efficacy of 1,2-dichlorobenzene and 1-methylnaphthalene as ^{13}C NMR solvents for fullerene analysis was demonstrated as well as the utility of 1,2-dichlorobenzene for the extraction of higher fullerenes from soot.

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Potent Solvents for C_{60} and their Utility for the Rapid Acquisition of ^{13}C NMR Data for Fullerenes

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27.

Potent Solvents for C_{60} and their Utility for the Rapid ^{13}C NMR Acquisition of Fullerenes

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Summary

Described are several solvents for the dissolution of fullerenes and the efficacy of 1,2-dichlorobenzene and 1-methylnaphthalene for obtaining fullerene ^{13}C NMR spectra.

A severe difficulty when working with fullerenes is that they are sparingly soluble in most common solvents, typically on the order of a few mgs mL^{-1}.[1,2] Solvents in which fullerenes are more soluble could be extremely useful for (1) exploring new fullerene reaction pathways, (2) developing new inexpensive purification methods for fullerenes,[3] (3) the extraction of higher fullerenes, and (4) facilitating ^{13}C NMR acquisition of the fullerenes and their derivatives. A number of groups have used carbon disulfide as an NMR solvent to get higher concentrations of fullerenes into solution.[4-6] High-boiling aromatic solvents such as 1,2,4-trichlorobenzene, quinoline, and 1,2,3,5-tetramethylbenzene have been used in extracting fullerenes from soot in order to give higher yields or to better extract the higher molecular weight fullerenes.[4,7,8] Recently, an investigation on the solubility of pure C_{60} in a number of common organic solvents was described.[9] With the exception of benzene, toluene, and carbon disulfide, all of the solvents reported were poorly solublizing (<1 mg mL^{-1}). Since benzene and toluene, both aromatic compounds, were among the best solvents reported, we investigated, and describe here, a number of common and not-so-common aromatic liquids to facilitate the dissolution and NMR acquisition of fullerenes.

Solubility data was obtained gravimetrically as follows. Approximately 5 mL of the appropriate solvent was added to an excess of C_{60} such that undissolved C_{60} always remained. The mixture was sonicated in a room temperature water bath for 30 min. The mixture was centrifuged for about 5 min and the solution at 24.5-25.5°C was then passed through a 0.45 µm HPLC syringe filter. Three 1.0 mL samples of this solution were removed and placed into pre-weighed vials. The vials were then placed into a heated oil bath (typically 100°C but 150°C oil bath was used for some of the higher boiling solvents) and solvent was gently removed via a stream of N_2. The vials were then cleaned of the exterior oil and weighed. The average of the three weights was recorded and a summary is presented in Table I.

The results indicate that many substituted aromatic solvents were superior to benzene and toluene for the dissolution of C_{60}. Substituted naphthalenes and 1,2-dichlorobenzene were approximately 10 times better solvents than toluene. Initial evaluation of the solubility data showed

Table I. Room Temperature Solubility of C_{60} in Various Solvent.[a]

SOLVENT	SOLUBILITY (mg mL^{-1})[b]	SOLUTION COLOR
benzene	1.5	magenta
toluene	2.9	magenta
ethylbenzene	2.6	magenta
n-propylbenzene	1.5	magenta
iso-propylbenzene	1.2	pink
n-butylbenzene	1.9	magenta
sec-butylbenzene	1.1	pink
tert-butylbenzene	0.9	pink
1,2-dimethylbenzene	8.7	magenta
1,3-dimethylbenzene	1.4	pink
1,4-dimethylbenzene,	5.9	magenta
1,2,3-trimethylbenzene	4.7	magenta
1,2,4-trimethylbenzene	17.9	magenta
1,3,5-trimethylbenzene	1.7	magenta[c]
1,2,3,4-tetramethylbenzene	5.8	magenta/brown
1,2,3,5-tetramethylbenzene	20.8	brown/yellow
fluorobenzene	1.2	pink
chlorobenzene	5.7	magenta
bromobenzene	2.8	magenta
iodobenzene	2.1	magenta
1,2-dichlorobenzene	24.6[d]	dark purple
1,2-dibromobenzene	13.8	magenta
1,3-dichlorobenzene	2.4	magenta
1,3-dibromobenzene	13.8	magenta
1,2,4-trichlorobenzene	10.4	magenta[e]
1-methylnaphthalene	33.2	brown/green
1-bromo-2-methylnaphthalene	34.8	brown
quinoline	7.2	brown
pyridine	0.3	pink[f]
thiophene	0.4	pink

[a] See text for the method of solubility determination. [b] Solubility data is approximately ±0.5 mg mL^{-1}. [c] An olive-drab-colored precipitate formed. [d] A value of 33 mg mL^{-1} was reported in ref 1. [e] A purple-black iridescent-colored precipitate formed. [f] Pyridine appeared to be reacting slowly with the C_{60}.[10]

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no readily obvious relationship between the solubility of C_{60} in a particular solvent and properties of the solvent. Moreover, a number of the solutions showed a distinct green or brown color which was different than the commonly observed magenta/pink/purple-colored solutions. In the case of 1,3,5-trimethylbenzene and 1,2,4-trichlorobenzene, unusual precipitates formed during sonication of the C_{60} mixtures. Complexes of C_{60} and benzene have been reported by the very slow crystallization of C_{60} from benzene solutions,[11] however, precipitate formation between C_{60} and 1,3,5-trimethylbenzene or 1,2,4-trichlorobenzene was unusually rapid and we are currently characterizing these unusual complexes/adducts. And not surprisingly, 1,2-dichlorobenzene is a superb solvent for the Soxhlet extraction of higher fullerenes from carbon arc soot.[12]

We then explored the efficacy of both 1,2-dichlorobenzene and 1-methylnaphthalene as ^{13}C NMR solvents (with 5% (v/v) C_6D_6 added for the internal deuterium lock signal) for a C_{60}/C_{70} mixture[2] (Fig 1) versus the spectra obtained in C_6D_6 as the only solvent.[13] All of the NMR samples were saturated with the fullerene mixture. Notice the dramatic increase in the signal to noise ratio for the spectra obtained in 1,2-dichlorobenzene and 1-methylnaphthalene as compared with C_6D_6 alone.[14] In Fig 1a, the C_{70} peaks in C_6D_6 can not even be resolved in the 28 min time period used for the analysis. Therefore, these solvents may prove to be particularly effective for obtaining the ^{13}C NMR spectra of the higher fullerenes which are generally less soluble than C_{60} and have less intense ^{13}C signals due to the range of magnetically dissimilar carbons. Note that the C_{70} peak at δ 132.7 ppm (not shown in Fig 1b but commonly observed at δ 130.9 ppm in C_6D_6) was coincident in chemical shift with one of the three 1,2-dichlorobenzene peaks.[13] Additionally, though 1-methylnaphthalene is a more potent solvent than 1,2-dichlorobenzene, there are small amounts of impurities present in the commercial material which add small impurity peaks to the ^{13}C NMR (Fig 1c, appearing upfield of the C_{60} peak). 1,2-Dichlorobenzene, however, is sufficiently free of other isomers and it only has three ^{13}C NMR signals, unlike the substituted naphthalenes. Additionally, the substituted naphthalenes are higher boiling than 1,2-dichlorobenzene making them more difficult to remove, and they are more reactive which may make them unsuitable for some reaction studies with the fullerenes. We are currently investigating the efficacy of these solvents for the purification of the higher fullerenes.

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Corporation, Ethyl Corporation, Shell Development Company, and Eli Lilly. W.A.S. thanks NASA and the American Vacuum Society for scholarships.

References and Notes

(1) During the completion of this manuscript, we were made aware of a similar yet complimentary study, by Dr. R. S. Ruoff, describing the solubility of C_{60} in 47 solvents. We thank Dr. Ruoff for sharing his data with us, in galley proof form, prior to its publication. See: Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, 00, 0000.

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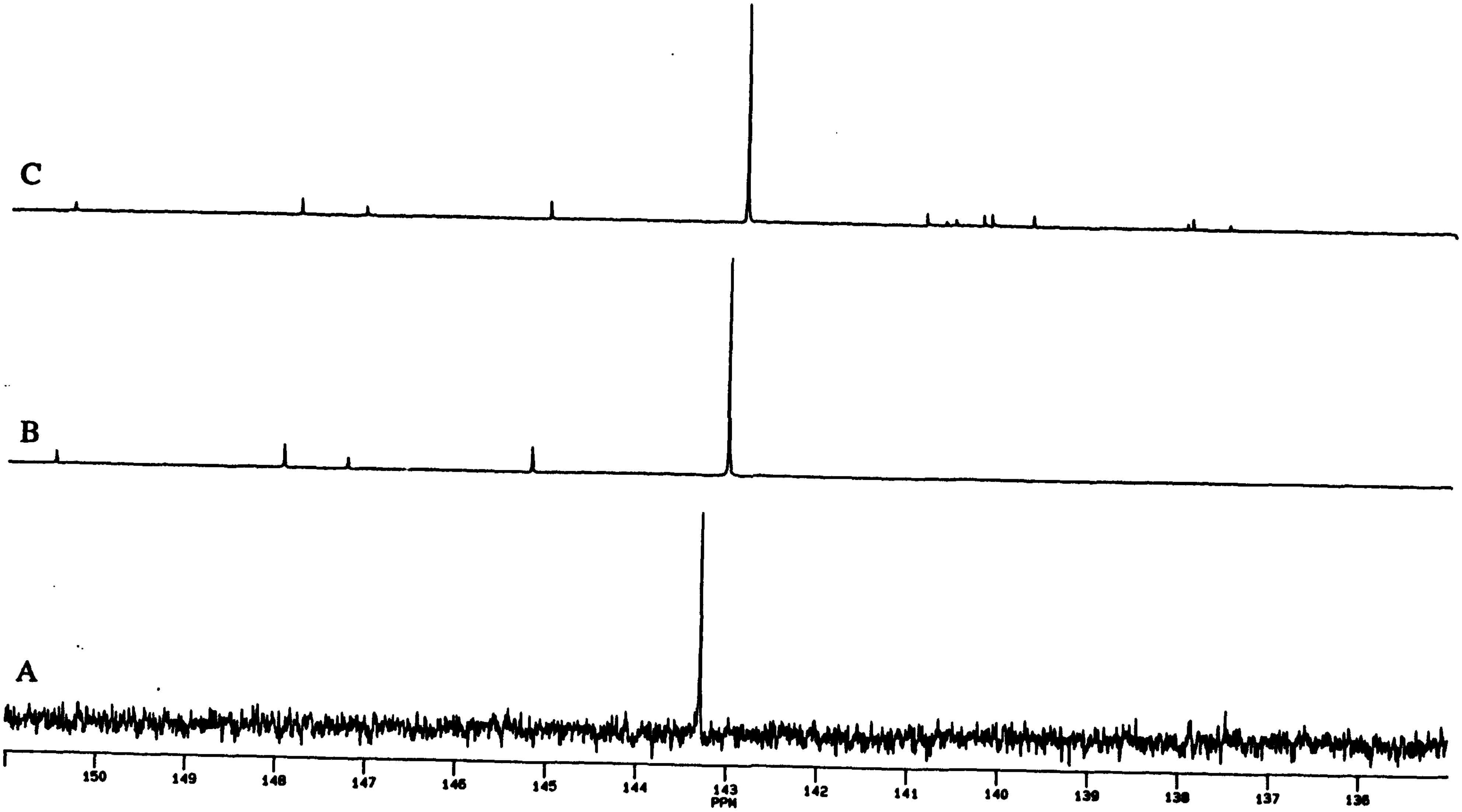
(12) Carbon arc-generated soot (7.74 g) was extracted with toluene via sonication for 1 h to yield 509 mg of extract. The soot was then further extracted with toluene using a Soxhlet extractor for 2 d to yield an additional 69 mg of extract. Further Soxhlet extraction of the soot with 1,2-dichlorobenzene afforded 95 mg of extract which was toluene insoluble and contained numerous higher fullerenes with up to C_{152} being clearly observed by mass spectrometry. See ref 7 for an analogous study using 1,2,3,5-tetramethylbenzene.

(13) The 1-methylnaphthalene resonances appear at δ 134.42, 134.23, 133.26, 128.99, 126.99, 126.92, 126.00, 125.90, 125.83, 124.50 ppm with 5% (v/v) C_6D_6 added for an internal deuterium lock signal. The 1,2-dichlorobenzene peaks appear at δ 132.68, 130.60, 127.86 ppm with the same C_6D_6 added.

(14) For the ^{13}C NMR of pure C_{60} saturated in 1-methylnaphthalene (plus 5% C_6D_6), 1,2-dichlorobenzene (plus 5% C_6D_6), and C_6D_6 only, the signal to noise ratios after 28 min of scanning were 790:1, 470:1, and 13:1, respectively.

(15) We optimized our ^{13}C NMR parameters by maximizing the signal to noise ratio on a sample of pure C_{60} in C_6D_6 by varying the pulse width. The optimal parameters (125 MHz) determined were: (a) pulse width = 2.0 μs, (b) pulse width for 90° tip ($\pi/2$) = 6.1 μs, (c) acquisition time = 1.704 s, and (d) delay = 0.005 s.

Fig 1. (a) 125 MHz ^{13}C NMR spectrum after 1024 scans (28 min) of a C_{60}/C_{70} mixture saturated in C_6D_6 as the only solvent. Signal to noise ratio equals 16:1. (b) The analogous spectrum after 1024 scans (28 min) of the same C_{60}/C_{70} mixture saturated in 1,2-dichlorobenzene with 5% (v/v) C_6D_6 added for an internal locking standard. Signal to noise ratio equals 295:1. (c) The analogous spectrum after 1024 scans (28 min) of the same C_{60}/C_{70} mixture saturated in 1-methylnaphthalene with 5% (v/v) C_6D_6 added for an internal locking standard. Signal to noise ratio equals 316:1.[14] See ref 15 for details of the optimized NMR parameters.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