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

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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 milligrams per litre.[1,2] Solvents in which fullerenes are more soluble could be extremely useful for (*i*) exploring new fullerene reaction pathways, (*ii*) developing new inexpensive purification methods for fullerenes,[3] (*iii*) the extraction of higher fullerenes and (*iv*) facilitating ^{13}C NMR acquisition of ^{13}C NMR data for the fullerenes and their derivatives. A number of groups have used carbon disulfide as an NMR solvent to get higher concentrations of fullerenes into

Table 1 Room temperature solubility of C_{60} in various solvents[a]

Solvent	Solubility/ mg ml^{-1b}	Solution colour
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 accuracy ca. ±0.5 mg ml^{-1}. [c] A drab olive precipitate formed. [d] A value of 33 mg ml^{-1} was reported in ref. 1. [e] A purple–black iridescent precipitate formed. [f] Pyridine appeared to be reacting slowly with the C_{60}.[10]

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 for better extraction of 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 the solvents reported were poorly solubilizing (<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 acquisition of NMR data of fullerenes.

Solubility data were obtained gravimetrically as follows. Ca. 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 a 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 1.

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 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 colour which was different from the commonly observed magenta–pink–purple solutions. In the case of 1,3,5-trimethylbenzene and 1,2,4-trichlorobenzene, unusual precipitates formed during sonication of the C_{60} mixtures. Formation of complexes of C_{60} and benzene has been reported by the very slow crystallization of C_{60} from benzene solutions;[11] however, formation of precipitates 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. Not surprisingly, 1,2-dichlorobenzene is a superb solvent for the Soxhlet extraction of higher fullerenes from carbon arc soot.[†]

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) and compared the spectra with those obtained in C_6D_6 as the solvent.[‡] All the NMR samples were saturated with the fullerene mixture. Noteworthy is the dramatic increase in the signal to noise ratio for the spectra obtained in 1,2-dichlorobenzene and 1-methylnaphthalene compared with C_6D_6 alone.[§] In Fig. 1(a), the C_{70} peaks in C_6D_6 cannot even be resolved in the 28 min 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 because they contain a range of magnetically dissimilar carbon atoms. Note that one of the C_{70} peaks [not shown in Fig. 1(b) but commonly observed at δ 130.9 in C_6D_6] was coincident in chemical shift with one of the three 1,2-dichlorobenzene peaks.[‡] 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 spectra [Fig. 1(c), 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.

[†] 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 days, 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.

[‡] 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 and 124.50 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 and 127.86 with C_6D_6 added.

[§] For the ^{13}C NMR spectra of a saturated solution of C_{60} 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.

[¶] 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 (π/2) = 6.1 μs, (c) acquisition time = 1.704 s, and (d) delay = 0.005 s.
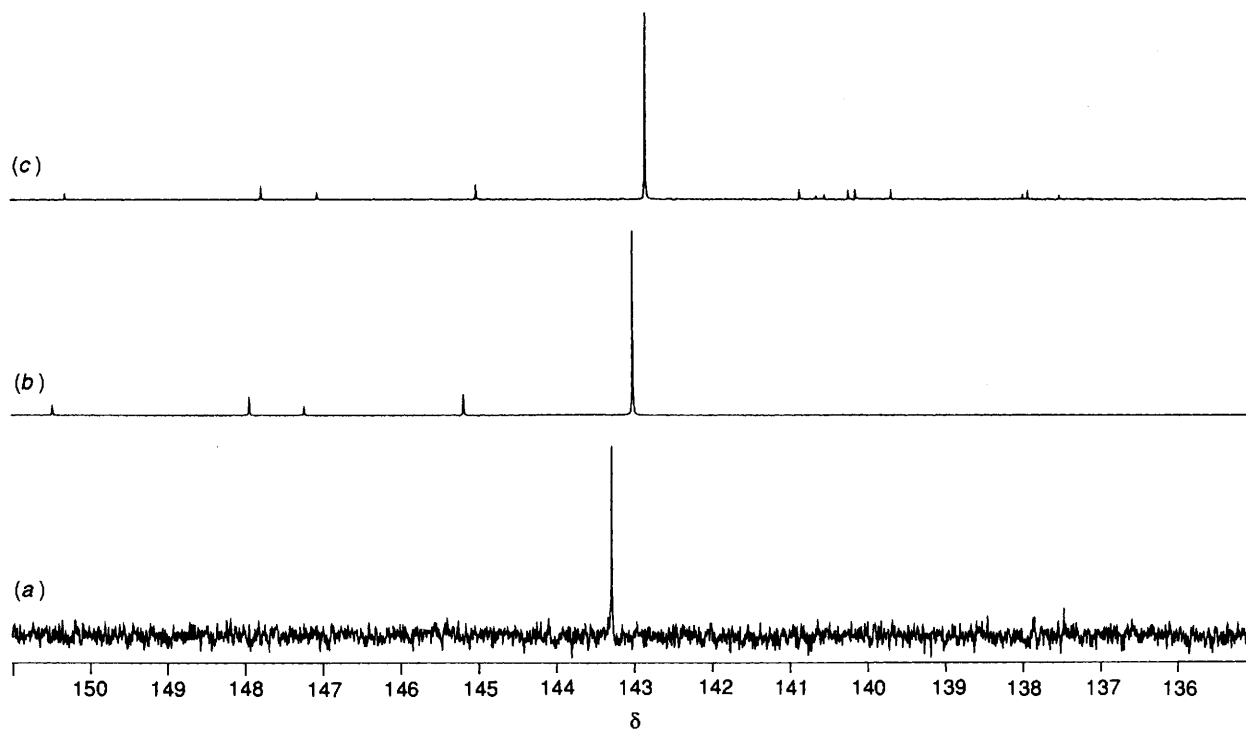
Fig. 1 (a) 125 MHz ^{13}C NMR spectrum after 1024 scans (28 min) of a C_{60}–C_{70} mixture saturated in C_6D_6 as the only solvent. Signal to noise ratio 16:1. C_{60} exhibits one ^{13}C NMR resonance at δ 143.29. C_{70} should exhibit five ^{13}C NMR resonances at δ 150.73, 148.18, 147.47, 145.43 and 130.94; however, owing to the poor signal to noise ratio in this spectrum, the C_{70} peaks are not observed. (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 lock. Signal to noise ratio 295:1. The C_{60} resonance appears at δ 143.02 while four of the five C_{70} resonances appear at δ 150.47, 147.93, 147.23 and 145.19. The highest field C_{70} peak appears beyond the chemical shift region shown but occurs coincident with one of the 1,2-dichlorobenzene peaks.‡ (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 lock. Signal to noise ratio 316:1. The C_{60} resonance appears at δ 142.85 while four of the five C_{70} resonances appear at δ 150.30, 147.78, 147.06 and 145.02. The highest field C_{70} peak appears beyond the chemical shift region shown and is obscured by the intense peaks of the 1-methylnaphthalene. The peaks appearing between δ 141–137 are due to impurities in the 1-methylnaphthalene.‡ See footnote § for ^{13}C NMR signal to noise ratios for pure C_{60} samples in the same three solvents used above. See footnote ¶ for details of the optimized NMR parameters.

References

1 During the completion of this work, we were made aware of a similar yet complementary study, by Dr R. S. Ruoff, describing the solubility of C_{60} in 47 solvents. We thank Dr Ruoff for a preprint: R. S. Ruoff, D. S. Tse, R. Malhotra and D. C. Lorents, *J. Phys. Chem.*, 1993, **97**, 3379.

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