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1. AGENCY USE ONLY (Leave blank) 2. REPORT DATE 11/22/93 3. REPORT TYPE AND DATES COVERED Technical Report

4. TITLE AND SUBTITLE Potent Solvents for C60 and their Utility for the Rapid Acquisition of 13C NMR Data for Fullerenes. 5. FUNDING NUMBERS G- N00014-89-J3062 R&T 4132084

6. AUTHOR(S) Scrivens, W. A.; Tour, J. M.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry and Biochemistry University of South Carolina Columbia, SC 29208 8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000 10. SPONSORING/MONITORING AGENCY REPORT NUMBER 27

11. SUPPLEMENTARY NOTES J. Chem. Soc., Chem. Commun., 1993, 1207.

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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 C60 up to 24.6 and 33.2 mg mL⁻¹, respectively. The solubility data was obtained gravimetrically. Precipitates were obtained when C60 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 C60. The efficacy of 1,2-dichlorobenzene and 1-methylnaphthalene as 13C NMR solvents for fullerene analysis was demonstrated as well as the utility of 1,2-dichlorobenzene for the extraction of higher fullerenes from soot.

4. SUBJECT TERMS 15. NUMBER OF PAGES 16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified 18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified 19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified 20. LIMITATION OF ABSTRACT UL

AD-A273 349



93-29298



1096

OFFICE OF NAVAL RESEARCH

GRANT : N00014-89-J-3062

R&T Code 4132084

Technical Report No. 27

Potent Solvents for C₆₀ and their Utility for the Rapid Acquisition of ¹³C NMR Data for Fullerenes

by

Scrivens, W. A.; Tour, J. M.

Accepted for Publication in

Journal of the Chemical Society, Chemical Communications

Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

November 22, 1993

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**Potent Solvents for C₆₀ and their Utility for the Rapid ¹³C NMR Acquisition of
Fullerenes**

Walter A. Scrivens and James M. Tour*

Department of Chemistry and Biochemistry

University of South Carolina

Columbia, South Carolina 29208

Summary

Described are several solvents for the dissolution of fullerenes and the efficacy of 1,2-dichlorobenzene and 1-methylnaphthalene for obtaining fullerene ¹³C 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 mg 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 ¹³C 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 C₆₀ 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 C₆₀ such that undissolved C₆₀ 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 N₂. 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 C₆₀. 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 C₆₀ in Various Solvent.^a

SOLVENT	SOLUBILITY (mg mL ⁻¹) ^b	SOLUTION COLOR
benzene	1.5	magenta
toluene	2.9	magenta
ethylbenzene	2.6	magenta
<i>n</i> -propylbenzene	1.5	magenta
<i>iso</i> -propylbenzene	1.2	pink
<i>n</i> -butylbenzene	1.9	magenta
<i>sec</i> -butylbenzene	1.1	pink
<i>tert</i> -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

^aSee text for the method of solubility determination. ^bSolubility data is approximately ± 0.5 mg mL⁻¹. ^cAn olive-drab-colored precipitate formed. ^dA value of 33 mg mL⁻¹ was reported in ref 1. ^eA purple-black iridescent-colored precipitate formed. ^fPyridine appeared to be reacting slowly with the C₆₀.¹⁰

no readily obvious relationship between the solubility of C₆₀ 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 C₆₀ mixtures. Complexes of C₆₀ 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} mixture² (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.

Acknowledgments. This research was funded by the Office of Naval Research, the National Science Foundation (EHR-91-08772, DMR-91-58315), and generous industrial contributors to the NSF Presidential Young Investigator Award (1991-96) for J.M.T.: Hercules Incorporated, IBM

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 C₆₀ 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.

(2) (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. (b) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(3) (a) Scrivens, W. A.; Tour, J. M. *J. Org. Chem.* **1992**, *57*, 6932. (b) Scrivens, W. A.; Bedworth, P. V.; Tour, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 7917.

(4) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science*, **1991**, *252*, 548.

(5) Diederich, F.; Whetten, R. L.; Thilgen, C.; Ettl, R.; Chao, I.; Alvarez, M. M. *Science*, **1991**, *254*, 1768.

(6) Taylor, R.; Langley, G. J.; Dennis, T. J. S.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Comm.* **1992**, 1043.

(7) Parker, D. H.; Wurz, P.; Chatterjee, K.; Lykke, K. R.; Hunt, J. E.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. *J. Am. Chem. Soc.* **1991**, *113*, 7499;

(8) Shinohara, H.; Sato, H.; Saito, Y.; Takayama, M.; Izuoka, A.; Sugawara, T. *J. Phys. Chem.* **1991**, *95*, 8449.

(9) Sivaraman, N.; Dhamodaran, R.; Kaliappan, I.; Srinivasan, T. G.; Rao, P. R. V.; Mathews, C. K. *J. Org. Chem.* **1992**, *57*, 6077.

(10) Hirsch, A.; Li, Q.; Wudl, F. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1309.

(11) (a) Geiser, U.; Kumar, S. K.; Savall, B. M.; Harried; S. S.; Carlson, K. D.; Mobley, P. R.; Wang, H. H.; Williams, J. M.; Botto, R. E.; Liang, W.; Whangbo, M. H. *Chem. Mater.* 1992, 4, 1077. (b) Meidine, M. F.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. *M. J. Chem. Soc., Chem. Comm.* 1992, 1534.

(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 C₁₅₂ being clearly observed by mass spectrometry. See ref 7 for an analogous study using 1,2,3,5-tetramethylbenzene.

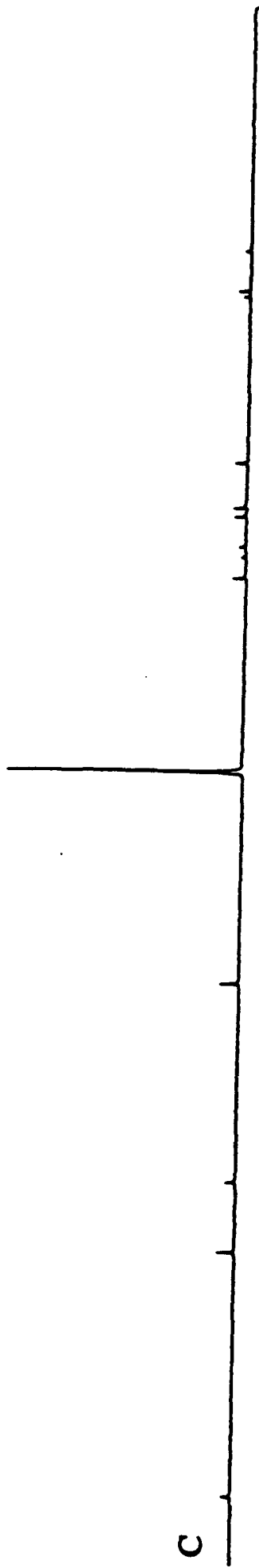
(13) The 1-methylnaphthalene resonances appear at δ 134.42, 134.23, 133.26, 128.99, 126.99, 126.92, 126.00, 125.90, 125.83, 124.50 ppm with 5% (v/v) C₆D₆ added for an internal deuterium lock signal. The 1,2-dichlorobenzene peaks appear at δ 132.68, 130.60, 127.86 ppm with the same C₆D₆ added.

(14) For the ¹³C NMR of pure C₆₀ saturated in 1-methylnaphthalene (plus 5% C₆D₆), 1,2-dichlorobenzene (plus 5% C₆D₆), and C₆D₆ only, the signal to noise ratios after 28 min of scanning were 790:1, 470:1, and 13:1, respectively.

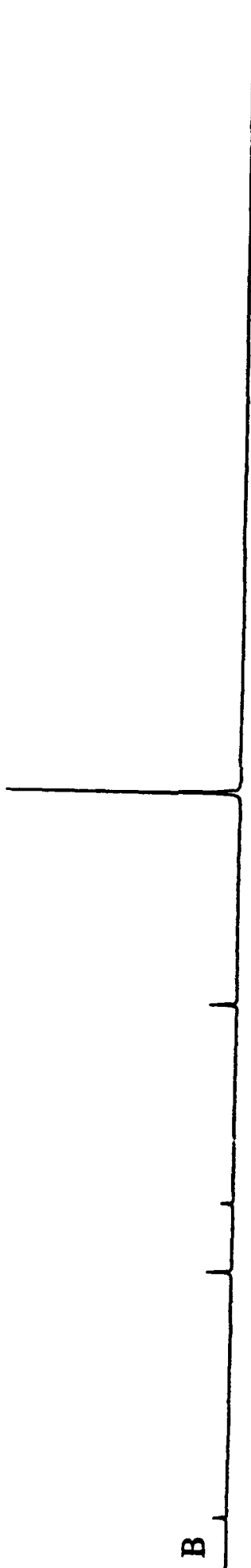
(15) We optimized our ¹³C NMR parameters by maximizing the signal to noise ratio on a sample of pure C₆₀ in C₆D₆ by varying the pulse width. The optimal parameters (125 MHz) determined were: (a) pulse width = 2.0 μ s, (b) pulse width for 90° tip ($\pi/2$) = 6.1 μ s, (c) acquisition time = 1.704 s, and (d) delay = 0.005 s.

Fig 1. (a) 125 MHz ^{13}C NMR spectrum after 1024 scans (28 min) of a $\text{C}_{60}/\text{C}_{70}$ 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 $\text{C}_{60}/\text{C}_{70}$ 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 $\text{C}_{60}/\text{C}_{70}$ 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.

C



B



A

