Experimental Evidence of Specific Solute–Solvent Interactions of Fullerenes C_{60} and C_{70} in Solution: One-Dimensional Steady-State Intermolecular ^{13}C, ^{1}H Overhauser Effect Study

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Steady-state one-dimensional selective intermolecular carbon-13, proton-1 NOE experiments provide the first experimental evidence of specific solute–solvent interactions of fullerenes C_{60} and C_{70} in solution. © 1998 Academic Press

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The recent success in generating macroscopic quantities of the C_{60} and C_{70} cluster (*1–4*) (Fig. 1) has stimulated intense interest and activity, and a variety of spectroscopic methods have been applied (*1–3, 5, 6*). In particular C_{60} may well be the most intensely researched single molecule in modern chemistry (*7*). The solubility of fullerenes in various solvents (*8–10*) may be of importance in rationalizing their reactivity, extraction, and chromatographic separation. However, to the best of our knowledge, no report investigating specific interactions of solvents with fullerenes at a molecular level has so far been published. Heteronuclear ^{13}C, ^{1}H Overhauser effect experiments can provide a valuable probe for investigating solute (^{13}C)–solvent (^{1}H) interactions (*11–15*). This Communication describes the application of a steady-state 1D selective intermolecular carbon-13, proton-1 NOE experiment and provides the first experimental evidence of specific solute–solvent interactions of fullerenes C_{60} and C_{70} in solution.

The ^{13}C NMR spectrum of C_{60} in *o*-dichlorobenzene, which is one of the best solvents for C_{60} with solubilizing capacity 10–15 times higher than that of benzene (*8, 9*), consists of a single line at 142.98 ppm (Figs. 2A, 2B). The spectrum of C_{70} consists of four lines at 150.45, 147.91, 147.20, and 145.16 ppm (Figs. 3A, 3B). A fifth peak at ~130.6 ppm, which is strongly overlapped with the solvent resonance, was assigned by Taylor *et al.* (*16*) to the equatorial ring of 10 carbon atoms e in analogy with the tertiary carbons in pyrene. The peaks at 145.16 and 147.91 ppm

arise from carbons d and c since models indicate carbons d to be less strained than carbon atoms c. Similarly, strain-induced hybridization changes have been utilized to assign the lines at 150.45 ppm and 147.20 ppm to types a and b carbon nuclei respectively (*16*). A 2D ^{13}C–^{13}C INADEQUATE analysis of C_{70} by Johnson *et al.* (*17*) has unequivocally confirmed the assignments made by Taylor *et al.* (*16*).

To build up the intermolecular heteronuclear NOE, selective low-power decoupling was applied on each pair of protons of *o*-dichlorobenzene followed by a high-power broadband composite decoupling during the observing pulse (^{13}C) and the acquisition of the free induction decay (*18, 19*). It is not trivial to define the optimum conditions of selective low-power decoupling in a multispin system in order to obtain NOE peaks of significant intensity. *o*-Dichlorobenzene is an $AA'MM'$ system ($J_{AM} \sim 6$ Hz), and the separation between the two multiplets (~105 Hz) is significantly larger than their overall widths. The spin system, therefore, is a case of strong coupling. The assignment of the H_3/H_6 multiplet ($\delta \approx 7.22$ ppm) and H_4/H_5 multiplet ($\delta \approx 6.96$ ppm) was based on the well-documented deshielding inductive effect of the chlorine atoms (*20*). The T_1 values of the H_4/H_5 and H_3/H_6 proton pairs, of the ^{12}C–^{1}H isotopomers, were measured by the inversion-recovery technique and were found to be 6.40 and 7.25 s respectively. The slightly faster relaxation of the H_4/H_5 protons is, very probably, due to the fact that these protons have two ortho partners, while H_3/H_6 have only one. Selective saturation of either multiplet can, therefore, be achieved by CW preirradiation of the solvent protons for 60 s with a decoupling band width $\gamma B_2 \approx 15$ Hz which shows good saturation efficiency and selectivity in measuring homonuclear NOEs. Heteronuclear NOE enhancement factors, f_c, were calculated from peak-height ratios after exponential multiplication and Fourier transformation. Thus $f_c = \{[I]_{NOE}/[I]_B\} - 1$, where the subscripts NOE and B refer to NOE spectrum and unperturbed spectrum, respectively.

Figure 2 shows a comparison of the ^{13}C, ^{1}H heteronuclear NOE experiments with the conventional 1D ^{13}C NMR spec-
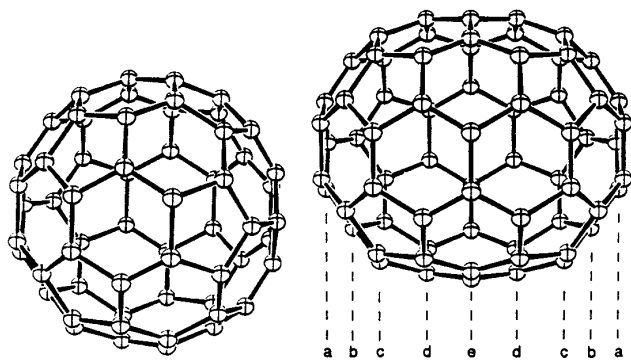
FIG. 1. Schematic diagram of fullerene-60 and fullerene-70 (based on the diagram in Ref. (5). The five sets of identical carbon nuclei a–e of C_{70} lie in the vertical planes as indicated.

trum of C_{60}. Solvent clustering around C_{60} is clearly demonstrated by the significant NOE peaks between the *o*-dichlorobenzene protons and the C_{60} carbons. The NOE peak intensity of the C_{60} carbons with the (4,5) pair of protons of *o*-dichlorobenzene, $f_c = 0.050$, is stronger than that of the (3,6) protons, $f_c = 0.035$, as is evident by the subtraction spectrum 2E. This would indicate closer orientation and, thus, stronger orthogonal $\sigma - \pi$ electronic interaction of the protons (4,5) of the solvent, which are remote to chlorine, with the π cloud of the ''aromatic'' C_{60} carbons. This preferential orientation should also be expected on the basis of the solvent dipole moment and the presence of partial negative charge on the chlorine atoms.

Indirect cross-relaxation effects, however, may complicate the interpretation of NOE data since saturation of, e.g., the H_4/H_5 protons obliterates cross-correlation terms involving this pair of spins, but cross-correlation terms for the remaining spin system are not eliminated (*18, 19*). Since heteronuclear NOE values resulting from saturation of the multiplets A, H_4/H_5, and M, H_3/H_6, can be quantified by

$$f'_c\{A\} = \frac{f_c\{A\} + f_c\{M\}f_M\{A\}}{1 - f_A\{M\}f_M\{A\}} \quad [1]$$

and

$$f'_c\{M\} = \frac{f_c\{M\} + f_c\{A\}f_A\{M\}}{1 - f_A\{M\}f_M\{A\}}, \quad [2]$$

it is important to investigate homonuclear NOE difference spectra resulting from on/off resonance selective irradiation of the A and M proton pairs. From Figs. 4B and 4C the enhancement factors $f_M\{A\} = 0.076$ and $f_A\{M\} = 0.049$ were calculated which provide a good indication that Eqs. [1] and [2] can be approximated as

$$f'_c\{A\} = f_c\{A\} \quad [3]$$

and

$$f'_c\{M\} = f_c\{M\}. \quad [4]$$

The difference in T_1 values of the H_4/H_5 and H_3/H_6 proton pairs would imply that the indirectly transmitted steady-state enhancement (*21, 22*) at H_3/H_6 on saturating H_4/H_5 will be larger than the steady-state enhancement at H_4/H_5 on
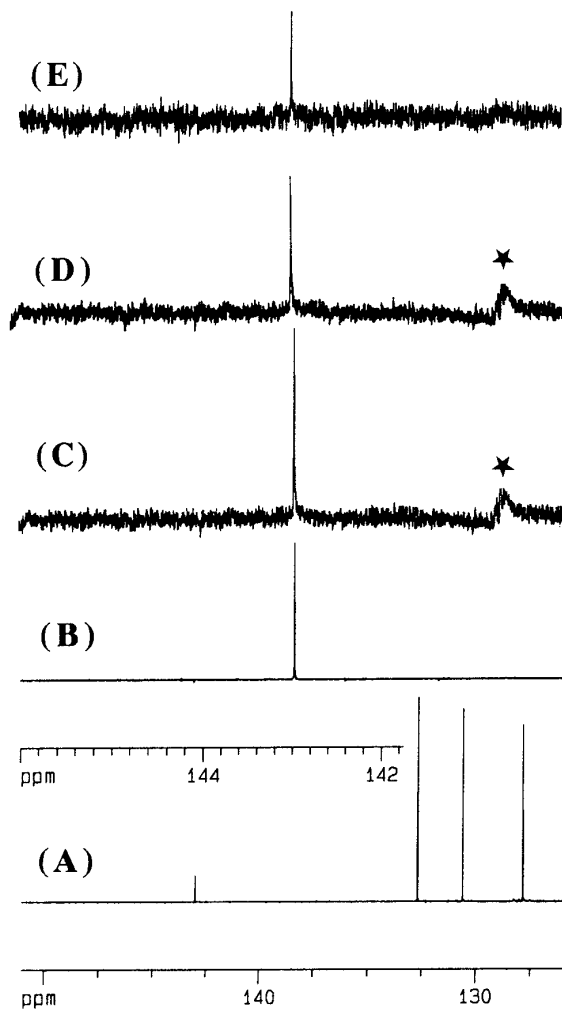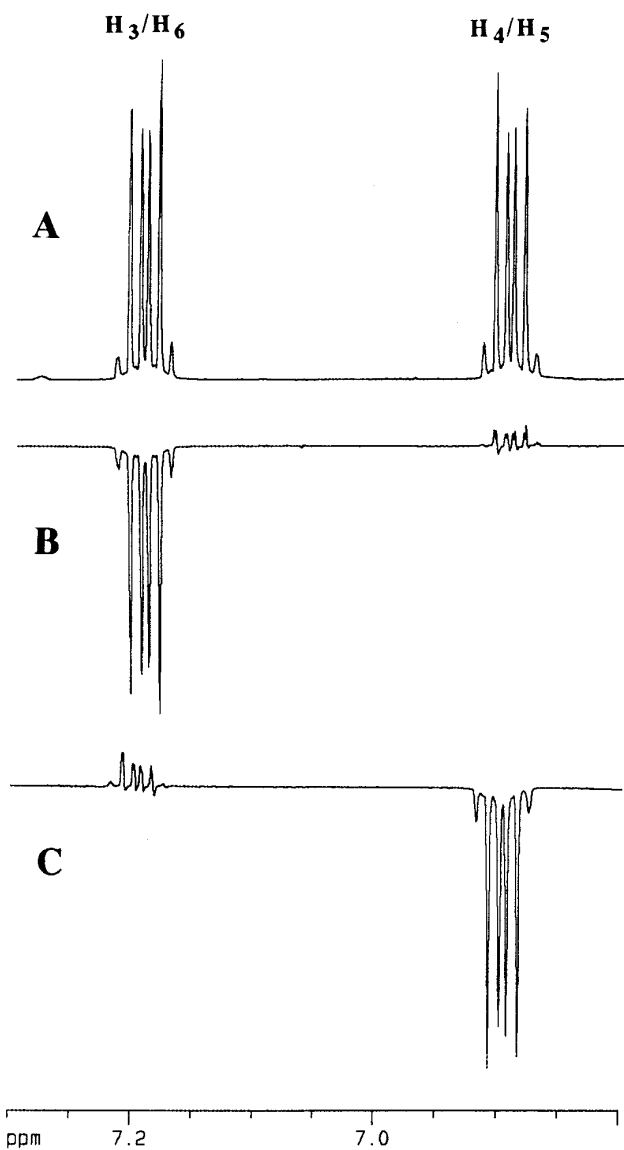

FIG. 2. (A) Conventional ^{13}C NMR spectrum of C_{60} in *o*-dichlorobenzene (90%)/C_6D_6 (10%) (concentration 22 mM) at 298 K, 5-mm sample tube, on a Brüker AMX 400-MHz instrument. Spectral acquisition parameters: 26 s acquisition time, 2.5 kHz spectral width, 74 s relaxation delay time, 120 scans. (B) Expanded region of the C_{60} carbons. (C) One-dimensional $^{13}C-{}^1H$ NOE difference experiment, 120 scans, 60 s selective low-power decoupling on the (4,5) pair of protons of o-dichlorobenzene, 14 s relaxation delay time. (D) As in (B) but with 60 s selective low-power decoupling on the (3,6) pair of protons. (E) The difference spectrum (C) − (D). The asterisk denotes a folded solvent resonance.

saturating H_3/H_6 which in turn would imply a larger (negative) indirect contribution to the intermolecular $^{13}C \{^1H\}$ NOE to the fullerene in the former case. This factor would reduce the difference between the enhancements seen on irradiating the H_4/H_5 proton pair and the H_3/H_6 proton pair, but not significantly.

The NOE peak intensities of the C_{70} carbons with the two pairs of protons of 1,2-dichlorobenzene indicate significant differences (Fig. 3). As is evident from the subtraction spectrum 3E, the (4,5) protons are closer and, thus, exhibit stronger orthogonal $\sigma - \pi$ electronic interactions with the π cloud of the C_{70} carbon atoms. This is in excellent agreement with the NOE data of the C_{60} fullerene. The ^{13}C spin–lattice
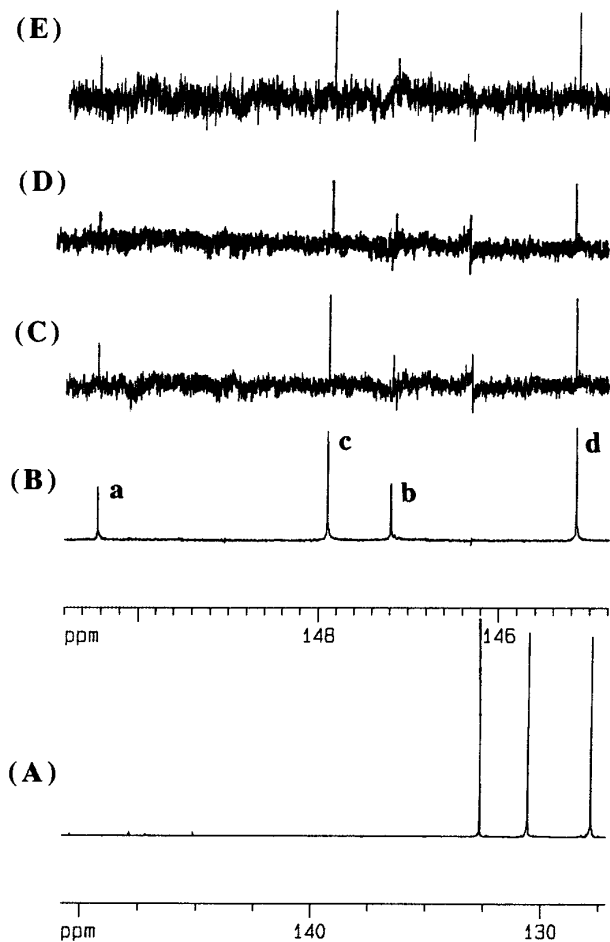
FIG. 3. (A) Conventional ^{13}C NMR spectrum of C_{70} in o-dichlorobenzene (90%)/C_6D_6 (10%) (concentration 21 mM) at 298 K, 5-mm sample tube, on a Brüker AMX 400-MHz instrument. Spectral acquisition parameters: 26 s acquisition time, 2.5 kHz spectral width, 74 s relaxation delay time, 1200 scans. (B) Expanded region of the a, b, c, and d carbons of C_{70}. (C) One-dimensional $^{13}C-^1H$ NOE difference experiment, 1200 scans, 60 s selective low-power decoupling on the (4,5) pair of protons of o-dichlorobenzene, 14 s relaxation delay time. (D) As in (B) but with 60 s selective low-power decoupling on the (3,6) pair of protons. (E) The difference spectrum (C) − (D).

FIG. 4. (A) Conventional ^1H NMR spectrum of the solution of Fig. 2A, at 298 K, on a Brüker AMX 400-MHz instrument. Spectral acquisition parameters: 17 s acquisition time, 240 Hz spectral width, 60 s relaxation delay time, 16 scans. (B) NOE difference spectrum resulting from selective CW preirradiation of the H_3/H_6 proton pair for 60 s with a decoupling band width $\gamma B_2 \approx 15$ Hz, 48 scans. (C) NOE difference spectrum resulting from selective CW preirradiation of the H_4/H_5 proton pair for 60 s with a decoupling band width $\gamma B_2 \approx 15$ Hz, 48 scans.

relaxation times of the C_{70} carbons are very similar (a, 30.6 s; b, 34.0 s; c, 33.4 s; and d, 31.2 s); therefore, they do not affect the specificity of the interactions. Further investigation, however, is needed to quantify NOE differences of the C_{70} carbons, particularly with respect to the π electron distribution, and thus aromaticity, for the different a–e sites in C_{70}. Minimal basis *ab initio* calculations (*23*) on C_{70} predict greatest diamagnetic shielding at the equator and least near the poles of this spheroidal cluster; however, the

absolute magnitudes of the total shieldings were found to be in very poor agreement with the experimental data.

In conclusion, the present findings are a demonstration of the utility of ^{13}C, ^{1}H NOE experiments as an effective probe for investigating interactions between fullerenes and solvents at a molecular level. Extension of these studies may be of importance in rationalizing the reactivity of fullerenes in different solvent media.

ACKNOWLEDGMENTS

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