NMR STUDY OF NON-EQUILIBRIUM STATE OF FULLERENE C_{60} IN *N*-METHYL-2-PYRROLIDONE

O.B. KARPENKO,[1] V.V. TRACHEVSKIJ,[2] O.V. FILONENKO,[1]
V.V. LOBANOV,[1] M.V. AVDEEV,[3] T.V. TROPIN,[3] O.A. KYZYMA,[4]
S.V. SNEGIR[1]

[1]**O.O. Chuiko Institute of Surface Chemistry, Nat. Acad. of Sci. of Ukraine**
(17, General Naumov Str., Kyiv 03164, Ukraine; e-mail: `ssnegir@gmail.com`*)*

[2]**G.V. Kurdyumov Institute for Metal Physics, Nat. Acad. of Sci. of Ukraine**
(36, Vernadskyi Ave., Kyiv 03142, Ukraine)

[3]**Joint Institute for Nuclear Research**
(6, Joliot-Curie Str., Dubna 141980, Russia)

[4]**Taras Shevchenko National University of Kyiv, Physical Faculty**
(4, Prosp. Academician Glushkov, Kyiv 03191, Ukraine)

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The results of ^{1}H NMR researches concerning the interaction between fullerene C_{60} and *N*-methyl-2-pyrrolidone (NMP) molecules in an as-prepared solution are reported. By comparing the spectra for pure NMP and the C_{60}-NMP system, system the formation of a complex between fullerene and solvent molecules is revealed, which is responsible for the time-dependent solvatochromic effect discovered earlier. Different magnitudes of chemical shifts for α-, β-, γ-, and α'-protons in the NMP molecules allowed a hypothesis to be put forward that the interaction in the C_{60}-NMP system occurs through the formation of a donor-acceptor bond between the keto-group of an NMP molecule and a fragment of a C_{60} molecule. The results of quantum chemical simulation for the $C_{60} \cdot$ NMP complex with a stoichiometric composition of 1:1 testify to a redistribution of the electron density over the system of bonds in an NMP molecule induced by a C_{60} molecule.

1. Introduction

Fullerene C_{60} is an allotropic modification of carbon with sp^2-hybridized orbitals. The C_{60} molecule has a cage structure, being rather resistant to the influence of external factors. In this connection, the interest to the study of its physico-chemical properties is unusually high [1–4]. It is especially concerns its solutions in highly polar media with the dielectric permittivity $\varepsilon \geq 10$, such as pyridine and *N*-methyl-2-pyrrolidone (NMP), in which the fullerene molecules tend to form clusters (aggregates) stable in time and various in dimensions (60–500 nm) [5–7]. The interaction between C_{60} molecules and solvents (or their mixtures) gives rise to the solvatochromic effect [8, 9], the magnitude of which changes in time. The solvatochromic effect manifests itself in optical [10], mass [11], and Raman [12, 13] spectra, as well as at the photoluminescence.

The origin of this effect may consists in the emergence of donor-acceptor bonds between electron-deficient C_{60} molecules [14, 15], on the one hand, and molecules of nucleophilic solvents [10], on the other hand. The C_{60} molecule was shown to be capable of forming complexes with organic molecules, which is accompanied by the charge transfer [16, 17]. Therefore, this work is a logic continuation of researches dealing with the association of fullerene molecules in the NMP medium with the dielectric permittivity $\varepsilon = 32$. Taking advantage of the ^{1}H nuclear magnetic resonance (^{1}H NMR) method, we carried out high-precision measurements of proton chemical shifts in an NMP molecule in the course of the $C_{60} \cdot (\mathrm{NMP})_x$ complex assembling. Quantum chemical calculations are performed to study the structural characteristics of the $C_{60} \cdot$ NMP complex and the energy of its formation.

2. Materials and Methods

For our researches, we used solutions of fullerene C_{60} (Fullerene Technologies, Russia; the purity degree is higher than 99.5%) in the NMP solvent (Merck; the purity degree is higher than 99.5%) with the addition of deuterized chloroform (R&D enterprise Ukrorgsintez, Ukraine; the purity degree is higher than 99.8%). The position of signals in NMR spectra were determined with respect to the reference signal of tetramethylsilane (Merck; the purity degree is higher than 99.7%).

The solutions were prepared by dissolving a crystalline powder of C_{60} for an hour with the use of a magnetic

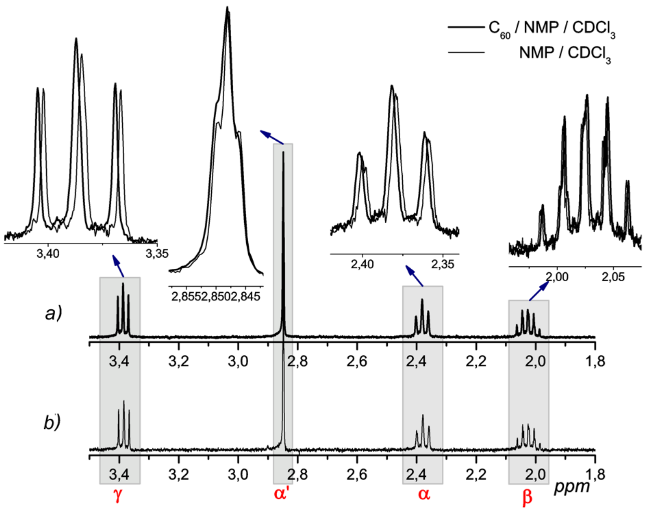


Fig. 1. NMR spectra of the initial NMP solution (*a*) and the solution NMP/C_{60} (*b*)

mixer. The absence of the solid phase was a visual criterion that fullerene had been dissolved. To exclude the influence of the C_{60} aggregation on the ^{1}H NMR parameters, we studied only as-prepared solutions of fullerene C_{60} in NMP.

To examine the features of complexing in the C_{60}-NMP system, we studied the ^{1}H NMR spectra of the following solutions:
1) C_{60} in $CDCl_3$ (1 mg/6 ml);
2) NMP in $CDCl_3$ (5 ml/1 ml);
3) C_{60} in $CDCl_3$ (5 mg/30 ml) + 1 ml NMP.
The volume of NMP added to the last solution was so chosen in order to reduce the excess of NMP molecules, which do not interact with the surface of a fullerene molecule.

^{1}H NMR spectra were registered at a frequency of 400.13 MHz, a specimen rotation rate of 20 Hz, and with the use of a one-pulse sequence (a pulse length of 12 μs and a delay of 2 s between pulses) in the accumulation regime.

The equilibrium spatial structures of C_{60} and NMP molecules were estimated in the framework of the semiempirical PM3 approximation. For their structural parameters and the complex formation energy to be determined more exactly, we used the density functional method with the exchange-correlation functional B3LYP and the basic set 3–21G**. The calculations were carried out with the help of software package PC GAMESS (version 7.1) [18]. The calculated values for the lengths of C–C bonds in a C_{60} molecule are quoted in Table 1. They correlate well with experimentally determined values [19], which confirms the adequacy of the method selected to solve the formulated problem.

Table 1. Lengths of C–C bonds (in nanometer units) in a C_{60} molecule

Bond	Experiment	DFT B3LYP 3–21G **
C–C (6.6)	0.140	0.139
C–C (6.5)	0.146	0.146

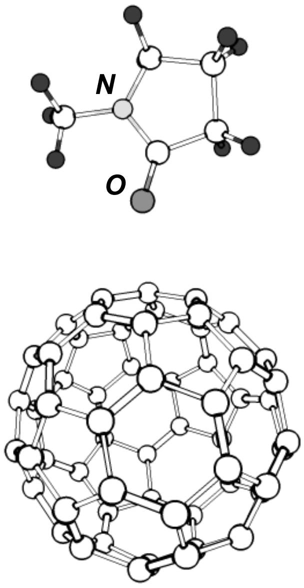


Fig. 2. Equilibrium structure of the $C_{60} \cdot$ NMP complex

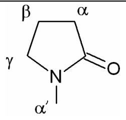
3. Results of Researches

We estimated the influence of fullerene on methyl (α') and methylene (α, β, γ) protons in NMP molecules (Table 2) by analyzing the spectra of C_{60} and NMP solutions in $CDCl_3$ (Table 2). Adding of fullerene C_{60} molecules into the NMP-$CDCl_3$ system results in a shift of signals from α-, γ-, and α'-protons toward lower fields, whereas the signal from β-protons shifts toward the strong field region.

The magnitudes of ^{1}H chemical shifts in NMP molecules correlate with the data obtained for the interaction between NMP and the surface of single-walled nanotubes [20]. An insignificant difference with the literature data may probably be associated with the differences between both the specimen temperatures [21] and the solution concentrations.

We also carried out a quantum chemical simulation of the spatial structure for the $C_{60} \cdot$ NMP complex. The NMP molecule was first arranged at a distance of 3.5 Å from the C–C (6,6) bond as the most reactive one [19].

Table 2. Magnitudes of chemical shifts (in ppm units) of protons in an NMP molecule

	α	$\Delta\alpha$	β	$\Delta\beta$	γ	$\Delta\gamma$	α'	$\Delta\alpha'$
NMP/CDCl$_3$	2.3797		2.0352		3.3877		2.8518	
C$_{60}$/NMP/ CDCl$_3$	2.3886	0.0089	2.0300	–0.0052	3.3940	0.0063	2.8560	0.0042

In the equilibrium structure of the $C_{60} \cdot$ NMP complex, the oxygen atom of the NMP molecule is located over the center of the hexagon fragment in the fullerene molecule (Fig. 2), which corresponds to the ^{1}H NMR data. The distance between the oxygen atom in the NMP molecule and the C_{60} molecule was equal to 3 Å after the optimization, and the formation energy for the $C_{60} \cdot$ NMP complex was determined to equal approximately to 0.2 eV (15.7 kJ/mol). An insignificant redistribution of the electron density (0.033 a.u.) from the *N*-NMP molecule onto the fullerene one takes place in the $C_{60} \cdot$ NMP complex. The obtained experimental ^{1}H NMR data and the corresponding theoretical calculations confirm our hypothesis concerning the formation of a donor-acceptor bond between the NMP keto-group and the surface fragment of a C_{60} molecule.

The results of our researches correlate with the spectrophotometric data for chloroform extracts of $C_{60} \cdot (\mathrm{NMP})_x$ complexes; namely, the absorption spectrum of the $C_{60} \cdot (\mathrm{NMP})_x$ complex keeps the properties of an intact fullerene C_{60} molecule, and the formation of the complex is induced by the non-covalent intermolecular coupling [10]. The presence of additional absorption peaks at 435 and 460 nm is inherent to complexes of C_{60} with *N*-methyl-polyvinilpyrrolidone with the charge transfer and testifies to a change in the electron state of fullerene C_{60} molecules at their transition into an *N*-methyl-2-pyrrolidone solution [22].

4. Conclusions

Hence, the changes in the chemical shifts of protons in an NMP molecule induced by the presence of a fullerene C_{60} molecule enables us to talk about the formation of the $C_{60} \cdot (\mathrm{NMP})_x$ complex. The difference in the magnitudes of chemical shifts for the α-, β-, γ-, and α'-protons in the NMP molecules points to the formation of a donor-acceptor bond between the keto-group of a solvent molecule (donor) and a fragment of a C_{60} molecule (acceptor), which is confirmed by the results of quantum chemical simulations as well.

1. P. Utko, R. Ferone, I.V. Krive, R.I. Shekhter, M. Jonson *et al.*, Nature Commun. **1**, 37 (2010).
2. T. Malaspina, E.E. Fileti, and R. Rivelino, J. Phys. Chem. B **111**, 11935 (2007).
3. S. Kurosu, T. Fukuda, Y. Shibuya, and T. Maekawa, Nanoscale Res. Lett. **6**, 80 (2011).
4. M.S. Liao, J.D. Watts, and M.J. Huang, J. Phys. Chem. B **111**, 4374 (2007).
5. M. Alfe, B. Apicella, R. Barbella, A. Bruno, and A. Ciajolo, Chem. Phys. Lett. **405,** 193 (2005).
6. V.L. Aksenov, M.V. Avdeev, T.V. Tropin, M.V. Korobov, N.N. Kozhemyakina *et al.*, Physica B **385–386**, 795 (2006).
7. R.G. Alargova, S. Deguchi, and K. Tsujii, J. Am. Chem. Soc. **123**, 10460 (2001).
8. S. Nath, H. Pal, and A.V. Sapre, Chem. Phys. Lett. **360**, 422 (2002).
9. S. Nath, H. Pal, and A.V. Sapre, Chem. Phys. Lett. **327**, 143 (2000).
10. N.P. Yevlampieva, Yu.F. Biryulin, E.Yu. Melenevskaja, V.N. Zgonnik, and E.I. Rjumtsev, Colloids Surf. A **209**, 167 (2002).
11. O.A. Kyzyma, M.V. Korobov, M.V. Avdeev, V.M. Garamus, S.V. Snegir *et al.*, Chem. Phys. Lett. **493**, 103 (2010).
12. I. Baltog, L. Mihut, M. Baibarac, N. Preda, T. Velula, and S. Lefrant, J. Opt. Adv. Mater. **7**, 2165 (2005).
13. I. Baltog, L. Mihut, M. Baibarac, N. Preda, T. Velula, and S. Lefrant, Rom. Rep. Phys. **57**, 837 (2005).
14. L.S. Wang, J. Conceicao, C. Changmingm, and R.E. Smalley, Chem. Phys. Lett. **182**, 5 (1991).
15. P.M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich *et al.*, J. Am. Chem. Soc. **113**, 1050 (1991).
16. C. Obondi1 and A.A. Rodriguez, Adv. Phys. Chem. **2010**, 102167 (2010).

17. J.D. Crane, P.B. Hitchcock, H.W. Kroto, R. Taylor, and D.R. Walton, J. Chem. Soc., Chem. Commun. **24**, 1764 (1992).
18. A. Granovsky, URL: http://lcc.chem.msu.ru/gran/gamess/index.html.
19. A.V. Eletskii and B.M. Smirnov, Usp. Fiz. Nauk **165**, 977 (1995).
20. D.J. Nelson, P.S. Nagarajan, C.N. Brammer, and P.T. Perumal, J. Phys. Chem. C **114**, 22 (2010).
21. Spectral Database for Organic Compounds, National Institute of Advanced Industrial Science and Technology (AIST), URL: http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi.
22. V.N. Zgonnik, L.V. Vinogradova, Yu.E. Melenevskaja, E.E. Kever, A.V. Novokhreshenova *et al.*, Zh. Prikl. Khim. **70**, 1538 (1997).

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ЯМР-ДОСЛІДЖЕННЯ НЕРІВНОВАЖНОГО СТАНУ ФУЛЕРЕНУ C_{60} В N-МЕТИЛ-2-ПІРОЛІДОНІ

О.Б. Карпенко, В.В. Трачевський, О.В. Філоненко,
В.В. Лобанов, М.В. Авдеєв, Т.В. Тропін,
О.А. Кизима, С.В. Снегір

Резюме

У роботі представлено результати дослідження взаємодії молекул фулерену C_{60} та N-метил-2-піролідону (NMP) у свіжоприготовленому розчині методом ЯМР ^{1}H. На підставі порівняння спектрів NMP та системи C_{60}-NMP виявлено комплексоутворення молекул розчинника та фулерену, що зумовлює виявлений раніше залежний від часу сольватохромний ефект. Зважаючи на різницю величин хімічного зсуву для α-, β-, γ- і α'-протонів молекул NMP припущено, що взаємодія в системі C_{60}-NMP відбувається шляхом формування донорно-акцепторного зв'язку між кетогрупою молекули NMP та фрагментом молекули C_{60}. Квантово-хімічне моделювання молекулярного комплексу $C_{60}\cdot$NMP стехіометричного складу (1:1) вказує на ініційований молекулою C_{60} перерозподіл електронної густини в системі зв'язків молекули NMP.