

MOLECULAR INTERACTION BETWEEN BENZONITRILE AND HEXAMETHYLPHOSPHORIC TRIAMIDE BY ^{13}C NMR T_1 RELAXATION TIME STUDIES AND *AB INITIO* QM CALCULATIONS: EXTENDED INVESTIGATION

Parsaoran Siahaan^{1*}, Cynthia L. Radiman², Susanto Imam Rahayu²,
Muhamad A. Martoprawiro², Dieter Ziessow³

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Bandung Institut of Technology. Jl. Ganesha 10 Bandung

²Inorganic and Physical Chemistry, Faculty of Mathematics and Natural Sciences,
Bandung Institut of Technology. Jl. Ganesha 10 Bandung

³Stranski Laboratory for Physical and Theoretical Chemistry TU Berlin

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ABSTRACT

It has been obtained the anisotropy ratio $\alpha = T_1(\text{ortho-,meta-}^{13}\text{C})/T_1(\text{para-}^{13}\text{C})$ of dilute solutions of *bn* change from 1.7 in *fa* solution and 1.5 in neat *bn* to 1.0 in HMPT. Thus the anisotropy ratio comes out to be $\alpha = 1$. In HMPT, obviously, solvent molecules cluster around $\text{Ph-C}\equiv\text{N}$ in such a way, that non-covalent interactions lead to isotropic reorientational motion like a spherical molecule. To conform with the T_1 times, a layer arrangement with at least two HMPT molecules per $\text{Ph-C}\equiv\text{N}$ seems to be likely. From computational quantum calculations of non-covalent intermolecular interactions and *Mie* potential analysis, the solute-solvent molecular pairs in *bn*···HMPT have almost equal interaction energies for the ortho, meta, and para configuration and the layered configurations are energetically permitted

Keywords: ^{13}C T_1 spin-lattice relaxation times, *ab initio* quantum chemistry calculations, intermolecular interactions, isotropic and anisotropic rotational motion

INTRODUCTION

Molecular interactions and motion are two interrelated physical phenomena which are important to be studied in order to explore and fully understand the properties of chemical systems and thereby their potential usefulness. Liquid crystals are a recent example. Already known for a century their potential remained undiscovered until only two decades ago when they were studied in more detail from the molecular viewpoint. Non-covalent intermolecular and intramolecular interactions, therefore, have become what is now intensively investigated to complement the advanced understanding of covalent interactions based on computational quantum chemistry.

Non-covalent interactions in fluid phases, although mostly being comparatively weak, lead to preferred structures of flexible large molecules and to molecular association between solute and solvent. Chemical bulk properties rest on such structuring which is specified in terms of molecular geometries and dynamics. Experimentally, NMR spectroscopy is a widely used method for the determination of structures and molecular dynamics in fluid phases. In this respect, studies of solute-solvent interaction by combining ^{13}C NMR T_1 spin-lattice relaxation investigations and *ab initio* quantum

theory on the molecular level can be considered as a relatively new research area.

The different melting point of benzene compounds group and its hydrogenation derivative explained by different molecular orientation [1] although these compounds group have almost similar mass. Woessner [2] and Huntress [3] studied the anisotropy effect on nuclear spin relaxation. Some relaxation mechanisms [4] which included the hydrogen study [5] by NMR were reported. The chemical system which studied by nuclear spin relaxation methods was increasing [6-9], included benzene and its derivative [7], and its theories also developed [10]. Factors such as steric effect on flexible molecule [11], delocalated electron spin effect through sigma bonding on relaxation [12] and hydrogen bonding effect on anisotropic reorientation [13] were studied. Study of benzene liquid relaxation was reviewed by Dolle [14]. The relaxation study was continued on simple system by synthesizing a compound model, although it had been applied on the more complex systems such as peptide [15].

This paper report the improvement of the previously result of non-covalent intermolecular behavior of benzonitrile (*bn*), $\text{Ph-C}\equiv\text{N}$ in HMPT mainly the result of computations [16]. Totally, research

* Corresponding author. Tel/Fax : +62-8179518965
Email address : s303saor@mail.chem.itb.ac.id

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focuses on the particularly interesting case of substituted benzenes which exhibit no internal rotational motion: phenylacetylene (**fa**), Ph-C≡CH, and benzonitrile (**bn**), Ph-C≡N which both have a triple bond in the substituent. The hydrogen atom of the -C≡C-H group was weakly acidic and positively charged. The nitrogen atom of -C≡N group is negatively charged. Whereas **fa** was known to form weak hydrogen bonds to proton acceptors, **bn** was devoid of such an attractive interaction yet has a larger electric dipole moment than **fa**. On the other hand, short range repulsive forces to a solvent molecule should be alike for **fa** and **bn** in view of their almost identical shape. Such a situation raises an important question: What local solute-solvent non-covalent structures built up in a mixture when the solvent molecule possesses a strong proton acceptor site or has no electric dipole moment at all. The appropriate choice for the first case was Hexamethylphosphoric triamide (HMPT), OP[N(CH₃)₂]₃. It was an exceptional solvent in that it has a large electric dipole moment but comparatively low dielectricity constant. This means that local structuring in dilute solutions of **fa** in HMPT was to be expected predominately due to the hydrogen bond -C≡C-H ... OP[N(CH₃)₂]₃. It is similar in shape to **fa** and **bn** but does not allow hydrogen bonding to HMPT. The questions: what the motion behavior and intermolecular interactions of **bn** in neat and HMPT? The results of ¹³C NMR T₁ relaxation times measurement and computations of **fa** in HMPT had been reported [17].

Eventually, phenylmethylacetylene, Ph-C≡C-CH₃ (**fma**) has also been included in the NMR measurements and will be reported in the next paper. It is similar in shape to **fa** and **bn** but does not allow hydrogen bonding to HMPT. The dilute solutions of **fa**, **bn**, and **fma** in **cy** serve as reference because **cy** has no electric dipole moment and a compact shape with internal mobility. Figure 1 shows the models of the studied molecules.

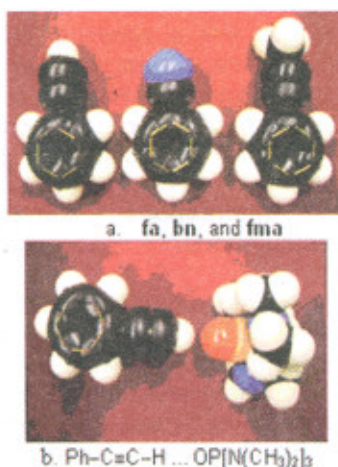


Figure 1. Models for the studied molecules and hydrogen bond **fa**...HMPT.

The conducted work comprises two main parts. (1) Experiments – to investigate the kind of rotational motion of the solute molecules **bn** by means of ¹³C T₁ relaxation times at ambient temperature as measured by inversion recovery sequence methods. And (2) Computations – to calculate the energy of intermolecular interactions by *ab initio* self-consistent field, Hartree-Fock (SCF-HF) quantum method.

The aims were to determine the effects of the substituents -C≡N on the rotational motion behavior of **bn** at high dilution in HMPT through the measured ¹³C T₁ relaxation times, and to ascertain the type of molecular association **bn**...HMPT by calculating the intermolecular interaction energy for various geometries.

EXPERIMENTAL SECTION

Material

All materials are from MERCK. Benzonitrile, Ph-C≡N, (**bn**; ρ=1; purity 99,9%), phenylacetylene (**fa**), Ph-C≡CH, (ρ=0,930; purity 98%), and hexamethylphosphoric triamide (HMPA), OP[N(CH₃)₂]₃ (ρ=1,030; purity 99%) were used.

Instruments

A set of distillation equipment, Mikro-KPG-Ubbelohde Viscometer and DMA 40 densitometer, a set of glasses and vacuum pump equipment, NMR Spectrometer of Bruker/Jeol 500 MHz, computer and a set of software such as Gaussian 03 and Mathcad were used.

Procedure

Experiment of ¹³C T₁ relaxation time by NMR.

Neat benzonitrile solution. Dynamic viscosity, η=ρv, was obtained after to measure kinematic viscosity, v, at 303 K. NMR spectrum was obtained by pulse methods at 302.5 K. Relative intensity, S_n(τ), of each peak with variation of pulse delay time, τ, was measured by pulse sequence π-τ-π/2 which is called *inversion recovery sequence* method [18]. ¹³C T₁ relaxation time each of C atom was calculated from the intercept value with τ axis graphic of S_n(τ) versus τ through Bloch equation [17].

$$M_z(\tau) = M_0 \{1 - 2e^{-\tau/T_1}\} \quad \text{or} \quad S_n(\tau) = A + B e^{-\tau/T_1} \quad (1)$$

Solution of benzonitrile in **fa and HMPA.** It was done similar to part (1) with in **fa** and HMPA solvent. The motion behavior in neat, **fa** and HMPT were figured as anisotropy ratio $\alpha = T_1(\text{ortho-}, \text{meta-}^{13}\text{C})/T_1(\text{para-}^{13}\text{C})$.

Table 1. ^{13}C T_1 relaxation times at 30.3 °C of solute benzonitrile, $\text{Ph-C}\equiv\text{N}$ (**bn**), in dilute solutions in **fa**, HMPT $\text{OP}[\text{N}(\text{CH}_3)_2]_3$, or neat (**bn**, **bn**).

Compounds / Carbon	^{13}C T_1 /s for		
	fa (0.93cP)	bn (1.20cP)	HMPT (4.08cP)
ortho- $\text{C}_{2,6}$	10.4	7.7	2.3
fa meta- $\text{C}_{3,5}$	11.6	7.6	2.3
para- C_4	6.6	5.1	2.3
(% molar)	(9.7)	neat	(8.9)

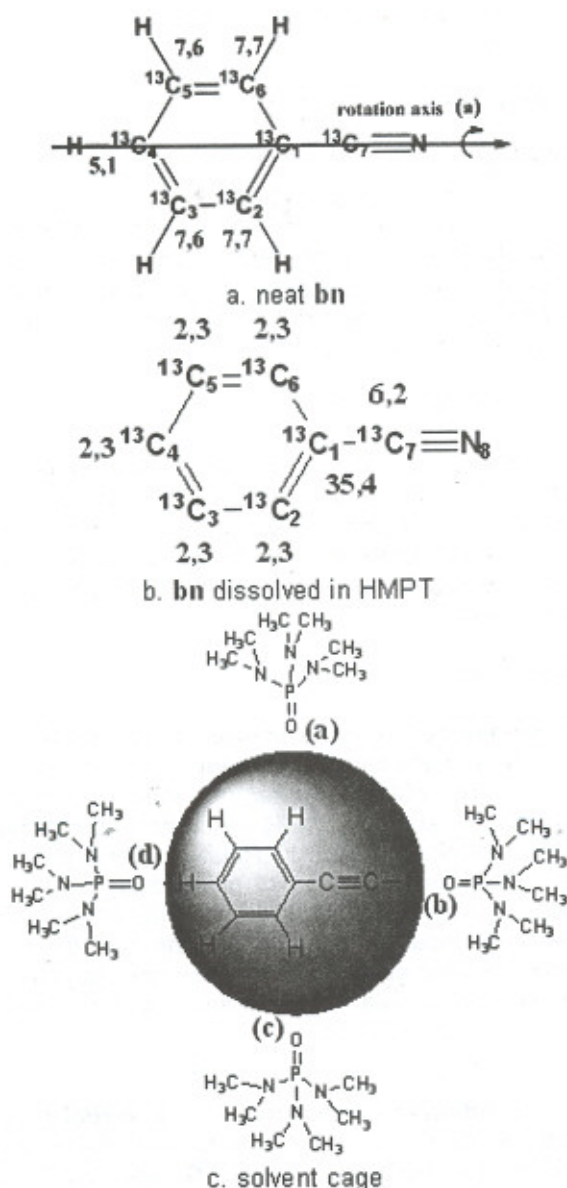


Figure 2. ^{13}C T_1 relaxation times in seconds in neat **bn** and the bond complex.

Computations

Firstly, molecular structure model of $\text{Ph-C}\equiv\text{N}$, HMPT, $\text{Ph-C}\equiv\text{N}\cdots\text{HMPT}$ complexes with various configuration were made. Z Matrix of each models were constructed. *Ab initio* calculations were performed with the theory and basis set of RHF/6-311G(d,p) with and without BSSE correction by counterpoise (CP) method for the single molecule **bn** as well as for various configurations of the solute-solvent molecular pair in diluted solution in HMPT. Energy of interaction will calculated as function of distance R by $\Delta E(R) = E_{AB} - (E_A + E_B)$ [17]. Interaction energies analysis by Mie potential and harmonic oscillator approach were calibrated with the calculated *ab initio* interaction energy. The result of calculation was interpreted to conform with the T_1 data.

RESULT AND DISCUSSION

Motion behavior by ^{13}C T_1 relaxation time

The sets of ^{13}C T_1 values were determined for the solutes **bn** in solvents **fa**, HMPT, and in neat **bn**. The solutions are less than 10 % mol except the cases **bn**, **bn** which was neat **bn**. On the average, a solute molecule was surrounded by the solvent molecule only. The experimental results were summarized in Table 1.

The ^{13}C T_1 values of **bn** in **fa** considerably shorter than in neat **bn**. This is basically a viscosity effect. Neat **bn** has a higher viscosity and the molar percentage of **bn** in **fa** is almost 10. In strong contrast to **fa**, the ^{13}C T_1 values of the ortho-, meta-, and para- ^{13}C nuclei of **bn** in dilute HMPT are equal to 2.3 s, Figure 2. Thus the anisotropy ratio comes out to be $\alpha = 1$.

This is an unexpected result in view of the shape similarity of **bn** and **fa**. In HMPT, obviously, solvent molecules cluster around $\text{Ph-C}\equiv\text{N}$ in such a way, that non-covalent interactions lead to isotropic reorientational motion like a spherical molecule. To conform with the T_1 times, a layer arrangement with at least two HMPT molecules per $\text{Ph-C}\equiv\text{N}$ seems to be likely. At any rate, firm conclusions are only possible with computational quantum calculations.

Intermolecular interactions energy by computational calculations

Figure 3 shows the type of energy of interaction calculated by formula $\Delta E(R) = E_{AB} - (E_A + E_B)$ without BSSE correction for **bn**...HMPT pairs.

Interaction energies analysis by Mie potential and harmonic oscillator approach were calibrated with the calculated *ab initio* interaction energy, Figure 3, resulting parameters of intermolecular interaction which

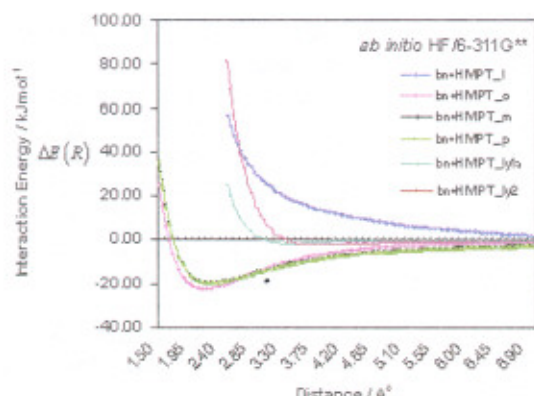


Figure 3. Intermolecular interaction energy in kJ/mol versus intermolecular distance for $\text{bn}\cdots\text{HMPT}$ pairs for linear (l), ortho (o), meta (m), para (p), and layered (ly) configuration in the range 1.50 – 7.00 Å.

Table 2. Equations of Mie potential calibration with and without counterpoise (CP) correction of various $\text{bn}\cdots\text{HMPT}$ pair configurations.

Configuration	Mie potential equation
$\text{bn}\cdots\text{HMPT}$ ortho	$V(R) = -4 \times 22.75 \left[\left(\frac{1.64}{R} \right)^{5.5} - \left(\frac{1.64}{R} \right)^{2.75} \right]$
$\text{bn}\cdots\text{HMPT}$ meta	$V(R) = -4 \times 18.69 \left[\left(\frac{1.64}{R} \right)^{5.5} - \left(\frac{1.64}{R} \right)^{2.75} \right]$
$\text{bn}\cdots\text{HMPT}$ para	$V(R) = -4 \times 19.83 \left[\left(\frac{1.70}{R} \right)^5 - \left(\frac{1.70}{R} \right)^{2.5} \right]$
$\text{bn}\cdots\text{HMPT}$ layered-1	$V(R) = -4 \times 16.78 \left[\left(\frac{1.70}{R} \right)^5 - \left(\frac{1.70}{R} \right)^{2.5} \right]$
$\text{bn}\cdots\text{HMPT}$ layered-2	$V(R) = -4 \times 19.86 \left[\left(\frac{1.70}{R} \right)^5 - \left(\frac{1.70}{R} \right)^{2.5} \right]$
$\text{bn}\cdots\text{HMPT}$ layered-1	$V(R) = -4 \times 15.53 \left[\left(\frac{3.05}{R} \right)^{12} - \left(\frac{3.05}{R} \right)^6 \right]^*$
$\text{bn}\cdots\text{HMPT}$ layered-2	$V(R) = -4 \times 2.42 \left[\left(\frac{3.34}{R} \right)^{10} - \left(\frac{3.34}{R} \right)^5 \right]^*$

* without counterpoise (CP) correction

is expressed in Mie potential, Table 2, and vibrational energy levels, Table 3.

The well depth ϵ of the Mie potential for $\text{bn}\cdots\text{HMPT}$ has the values -18.69, -16.78, and -16.85 for the ortho, meta, and para association. They have almost equal interaction energies as the dominant association, Figure 4. Analysis Mie potential by oscillator approach gives the respective values for the ground state energy are 0.78, 0.62, and 0.63 kJ/mol , and 64.91, 47.80, and 41.85 Nm^{-1} for the vibrational constant which indicate the stable association compare to layered association which also permitted, as shown in Table 3.

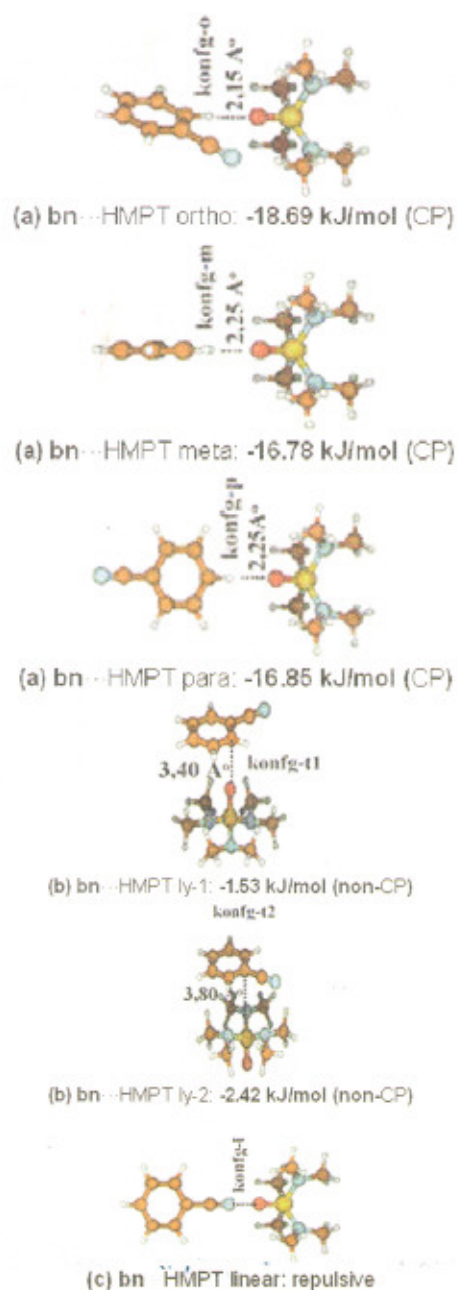


Figure 4. (a) The dominant, (b) less dominant and (c) forbidden association of $\text{bn}\cdots\text{HMPT}$.

CONCLUSION

The solute-solvent molecular pairs in $\text{bn}\cdots\text{HMPT}$ have almost equal interaction energies for the ortho, meta, and para configuration and the layered configurations were energetically permitted. The $\text{bn}\cdots\text{HMPT}$ form stable associates. These findings comply with the calculated vibrational energy levels and vibrational constant.

Table 3. Vibrational energy levels in kJ/mol with and without counterpoise (CP) correction of various bn...HMPT pair configurations with the theory basis set HF/6-311G** by Mie potential analysis.

	Ortho	Meta	Para	Ly.-1	Ly.-2
	Mie- 5.5,2.75	Mie- 5, 2.5	Mie- 5,2.5	LJ- 12,6	Mie- 10,5
$E_{v=15}$		20.95	20.96		
$E_{v=14}$		19.59	19.61		
$E_{v=13}$	22.90	18.24	18.25		
$E_{v=12}$	21.21	16.89	16.90		
$E_{v=11}$	19.51	15.54	15.55		
$E_{v=10}$	17.81	14.19	14.20		
$E_{v=9}$	16.12	12.84	12.85		
$E_{v=8}$	14.42	11.49	11.49		
$E_{v=7}$	12.72	10.13	10.14		
$E_{v=6}$	11.03	8.78	8.79		
$E_{v=5}$	9.33	7.43	7.44		
$E_{v=4}$	7.63	6.08	6.08		1.93
$E_{v=3}$	5.94	4.73	4.73	1.48	1.38
$E_{v=2}$	4.24	3.38	3.38	0.89	0.83
$E_{v=1}$	2.54	2.03	2.03	0.30	0.28

* Without counterpoise (CP) correction,
ly – layered, LJ – Lennard Jones.

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