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

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ABSTRACT

Intermolecular interactions and molecular translational and rotational mobility are key factors in molecular material sciences, e.g. liquid crystals. One of the important substructures is given by phenylacetylene, Ph-C≡CH. Its rotational behavior in its pure form and in high dilution in hexamethylphosphoric triamide OP[N(CH$_3$)$_2$]$_3$ (HMPA) has been studied by means ^{13}C NMR T_1 relaxation times at ambient temperature as measured by the inversion recovery method. HMPA is an exceptional solvent in that is has a quite large dipole moment but comparatively low relative dielectricity constant. From the molecular shape Ph-C≡CH is expected to exhibit anisotropic rotational diffusion which in fact can be deduced from the measured set of T_1 values of the ortho, meta and para carbon nuclei in the neat liquid as well as in the HMPA solution. This expected result rules the dominance of a linearly molecules pair Ph-C≡CH…HMPA along their dipole moment axes as anticipated in view of the large HMPA dipole moment. In order to conform with the T_1 data, a linear arrangement of Ph-C≡CH via the interaction between its weakly acidic H-atom with negatively charge O-atom of HMPA molecules seems to lead to such an anisotropic rotational motion. This hypothesis is supported by ab initio QM calculations which come out with higher interaction energy for linear orientation than other geometries. These ab initio calculations were performed with the basis set of RHF/6-31G(d) for the single molecules of Ph-C≡CH and HMPA as well as for their various geometries of the molecules pair. Molecular dynamics simulations need to be performed for further confirmation.

***Keywords**: Relaxation Times, HMPA, pheylacetylene, ab initio, intermolecular interaction, rotational diffusion*

INTRODUCTION

To increase the beneficiaries of the information involved in NMR spectroscopy whether as images (in magnetic resonance imaging, MRI) or spectra it can be done by understanding of spin-lattice and spin-spin relaxation times. The mainly mechanism one of spin-lattice relaxation is ^{13}C-^{1}H dipole-dipole or dipolar interaction. So, molecular dynamics properties of local and the whole structure that partly determine the properties of the system are obtained by NMR method, which are known through the information that is indicated on the reorientation behaviour of dipole-dipole vector of nuclear spin in which one of them is ^{13}C-^{1}H dipole-dipole. That information included in a data which is called ^{13}C NMR T_1 relaxation times. Measurement of spin-lattice relaxation times can give the information of molecular dynamics. Because of the interaction can affect molecular dynamics, then this interaction can also be known from ^{13}C-^{1}H dipole-dipole orientation of nuclear spin. If two or more of molecule interact, it will form what is called paired-molecule. It can be between solute-solute, solute-solvent, and solvent-solvent. The preferred paired-molecule of this interaction becomes the key factor to determine the solution structure. In pairing-molecule, molecular polarity is important. Polarity can affect interaction energy, geometry, and its symmetry. Therefore, molecular geometry and symmetry of paired-molecule can be determined from ^{13}C-^{1}H dipole-dipole reorientation of nuclear spin.

The different of melting point between benzene and its derivative of hydrogenation had been explained by different molecular orientation caused by different symmetry [1] although this compounds group has almost similar mass. Woessner [2] and Huntress [3] studied the effect of anisotropy on nuclear spin relaxation. Some of relaxation mechanisms were reported [4,5] which included the study of hydrogen bonding by NMR [6]. The amount of chemical system which was studied by nuclear spin relaxation methods was increasing [7-10], benzene and its derivative included [8], and its theories also developed [11]. Some of factors such as steric effect on flexible molecule were studied [12], delocalised electron spin effect through sigma bonding on relaxation [13] and hydrogen bonding effect on anisotropic reorientation [14].

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Although benzene liquid relaxation was studied, it was reviewed by Dolle [15]. The relaxation study was continued on simple system by synthesizing a compound model, although it had been done on more complex systems such as peptide [16].

Since molecular rotational dynamic sensitively is affected by their chemical environment, therefore, in order to obtain more accurately result of studies it is selected the molecule which has the mobility not too flexible and complex. For this purpose an appropriate molecule is monosubstituted benzene compounds. Phenylacetylene**,** Ph-C≡CH, which has a weakly acidic hydrogen, theoretically it can interact through oxygen with hexamethylphosphoric triamide (HMPA), $OP[N(CH_3)_2]3$. Based on these theoretically assuming properties of interaction, phenylacetylene in HMPA will show the anisotropic rotation motion, and it is interest to investigate whether it is.

Is there interaction between Ph-C≡CH and HMPA through acidic hydrogen of Ph-C≡CH with oxygen of hexamethylphosphoric triamide (HMPA)? What is effect of this interaction on rotational motion of Ph-C≡CH? Ph-C≡CH molecule has phenyl group which has similar structure with benzene, it is rigid and low flexibility. From the molecular shape, Ph-C≡CH is expected to exhibit anisotropic rotational diffusion. HMPA molecule is an exceptional solvent in that is has a quite large dipole moment but comparatively low relative dielectricity constant. Therefore, Ph-C≡CH molecule has a weakly acidic hydrogen which can linearly interact with HMPA. Then it is interest and important to investigate this kind of interaction. Whether the interaction through acidic hydrogen just only one possibility of configuration? In order to know which are the configurations are preferred, the Ph-C≡CH molecule in neat and in HMPA both will be investigated by ^{13}C NMR spectroscopy. The data of relaxation time T_1 will be determined and interpreted. Based on the pattern of relaxation time T_1 the appropriate configurations of interaction between Ph-C≡CH and HMPA will be obtained.

In order to support the result of NMR measurement, energy of interaction will calculated by *ab initio* methods. Interaction energy will calculated by formula $\Delta E_k = E_{kAB} - (E_A + E_B)$ [17]. The preferred configurations of interaction between molecule Ph-C≡CH and HMPA are determined based on the lowest energy of each their paired-molecule. The objective is investigation a deeper understanding of the behaviour of rotational motion of phenylacetylene molecule in HMPA solution through determination of T_1 ^{13}C spin-lattice time relaxation.

EXPERIMENTAL SECTION

Materials

All materials are for NMR spectroscopy from MERCK. Phenylacetylene (pa), Ph-C≡CH, (ρ=0.930; purity 98%), hexamethyl-phosphoric triamide (HMPA), $OP[N(CH_3)_2]_3$ (ρ=1,030; purity 99%), solution 3% phenylacetylene in HMPA.

Instrumentation

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 and Jeol 500 MHz, respectively, a set of software such as Gaussian 03 and Mathcad for calculation and analysis were used.

Procedure

Experiment of T_1 ^{13}C relaxation time by NMR

Neat phenylacetylene solution non-degassed

Dynamic viscosity, η=ρv, was obtained after to measure kinematics viscocity, v, at 303 K. NMR spectrum was obtained by *pulse* methods at 302.5 K. Relative intensity, Sn(τ), of each ^{13}C nuclei peak with variation of pulse delay time, τ, was measured by pulse sequence π-τ-π/2 which is called *inversion recovery sequence* method [17]. T_1 ^{13}C relaxation time each of carbon atom was calculated from the intercept value with τ axis graphic of Sn(τ) versus τ through Bloch equation,

$$M_z(\tau) = M_o\left\{1-2e^{-\tau/T_1}\right\} \quad \text{or} \quad S_n(\tau) = A + Be^{-C\tau} \quad ....(1)$$

Solution of phenylacetylene in HMPA non-degassed

It was done similarly to part **(1)** with in HMPA solvent.

Calculation molecular geometry

Firstly, molecular structure model of single molecule: Ph-C≡CH, HMPT, paired-molecule: Ph-C≡CH...Ph-C≡N, Ph-C≡CH...HMPT, with various configurations were made. Matrix Z of each models were constructed. Then, calculating of molecular geometry optimation was done by *ab initio* at theory level RHF/6-31G(d). The result of calculation was interpreted to confirm the T_1.

RESULT AND DISCUSSION

Determination of T_1 ^{13}C relaxation time

Neat phenylacetylene solution non-degassed

The T_1 time relaxation of carbon C_1, $C_{2,6}$, $C_{3,5}$, C_4, C_7 and C_8 of neat phenylacetylene, Fig 3, was obtained In other word, it was happened interaction between phenylacetylene and HMPA molecule. Reduction was higher than four times in C_4 and C_8. The reduction of relaxation time was happened only if paired-molecule between phenylacetylene molecule and HMPA was

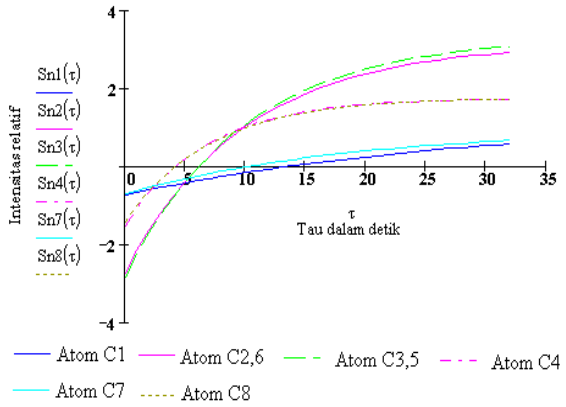

Fig 1. Curve of Sn versus τ for neat phenylacetylene

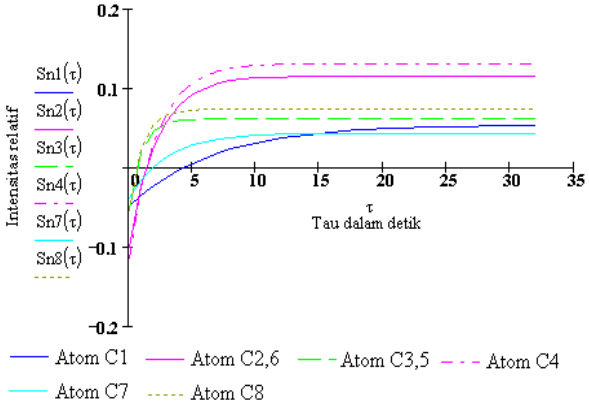

Fig 2. Curve of Sn versus τ for solution phenylacetylene in HMPT

Table 1. $T_1{}^{13}$C Relaxation time of neat phenylacetylene and solution in HMPT

Carbon	$T_1{}^{13}$C/second	
	Neat	In HMPT
C_1	28,1817	6,6154
$C_{2,6\ (ortho)}$	9,8602	2,2281
$C_{3,5\ (meta)}$	9,8644	2,1764
$C_{4\ (para)}$	6,7179	1,0232
C_7	18,5519	2,9354
C_8	7,0550	1,0502

occurred. Therefore, $T_1{}^{13}$C relaxation time data by using equation-1 as an exponential regression was given in Fig 1. Data of T_1 time relaxation listed in column 2 Table 1. Whereas the T_1 time relaxation of carbon C_1, $C_{2,6}$, $C_{3,5}$, C_4, C_7 and C_8 of phenylacetylene in HMPT, was obtained by using equation-1 as an exponential regression of Fig 2. Data of T_1 time relaxation listed in column 2 Table 1.

In neat phenylacetylene the carbon nuclear C1 and C_7 have $T_1{}^{13}$C relaxation time longer than other where there is no hydrogen directly bonded. Whereas the similar $T_1{}^{13}$C relaxation time of orto and meta

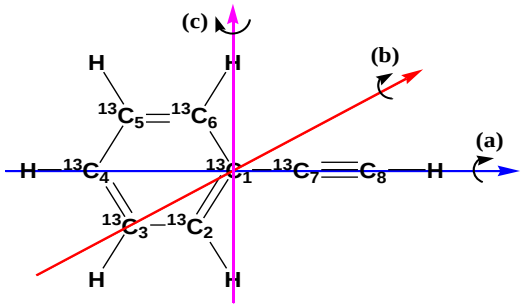

Fig 3. Three possibility of rotation axis of phenylacetylene molecule

Table 2. The *ab intio* calculation of single and paired-molecule between phenylacetylene and HMPA

Molecule	Energy E/Hartree	ΔE_k/ kcal.mol^{-1}
Single:		
1. pa	-306,3783	-
2. HMPA	-816,5731	192,255.10^3
paired:		
pa…pa	-612,7577	-0,7530
pa…HMPT linear	-	-50,8041
pa…HMPT orto	1123,0323	-49,3167
pa…HMPT meta	-	-48,9407
pa…HMPT para	1123,0299	-48,9829
pa…HMPT	-	-47.2502

Molecule	Dipole moment μ/Debye	Interaction distance r/A^o
1. pa	0,6893	
2. HMPA	1,9926	
pa…pa	0,0004	3,1726
pa…HMPT linear	4,9521	($r_{3,15}$)
pa…HMPT ortho	4,2139	2,1408
pa…HMPT meta	-	2,4200
pa…HMPT para	6,0083	-
pa…HMPT	-	2,3863

9,8602 and 9,8644 second, respectively, indicate the similar ^{13}C-H vector orientation with static magnet field B_o. This happened if the Ph-C≡N molecule, Fig 3, rotate in parallel axis (a) with -C≡CH substituen.

Solution phenylacetylene in HMPA non-degassed

The $T_1{}^{13}$C relaxation time of carbon atom $C_{2,6}$, $C_{3,5}$, C_4 was obtained included in column-3 Table 2. The $T_1{}^{13}$C relaxation time in HMPA solution was highly reduced. In HMPA solution the $T_1{}^{13}$C relaxation time of carbon nuclear $C_{2,6}$ and $C_{3,5}$, reduced average approximately four times. Instead of their hydrogen directly bonded, the reduced of relaxation time indicate the lower mobility of phenylacetylene molecule.

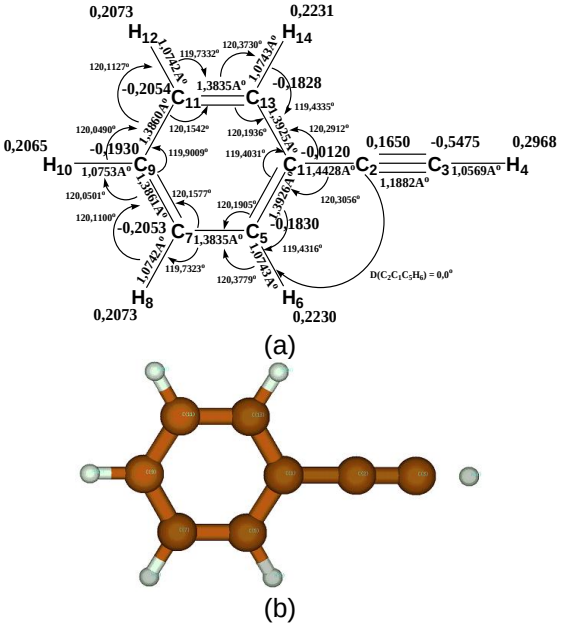

Fig 4. Molecular geometry of phenylacetylene (a) values of parameters, (b) tree-dimensional structure.

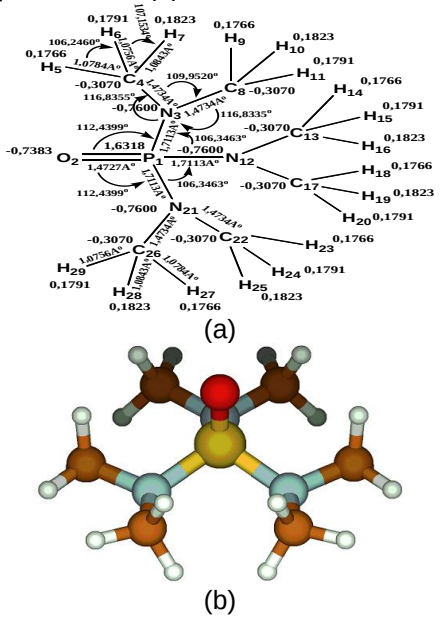

Fig 5. Molecular geometry of HMPT (a) values of parameters, (b) tree-dimensional structure

suggested to forming Ph-C≡CH...HMPApaired-molecule. From the molecular shape Ph-C≡CH is expected to exhibit anisotropic rotational diffusion which in fact can be deduced from the different set of T_1 values. In HMPA solution this set of T_1 values of the ortho, meta and para carbon nuclei was also exhibit anisotropic rotational diffusion. It means the reorientation motion of phenylacetylene is anisotropic. If this is happened the paired-molecule seem lead to linearly shaped molecule. From the view of molecular shape of phenylacetylene and HMPA, which will also be calculated by *ab initio*,

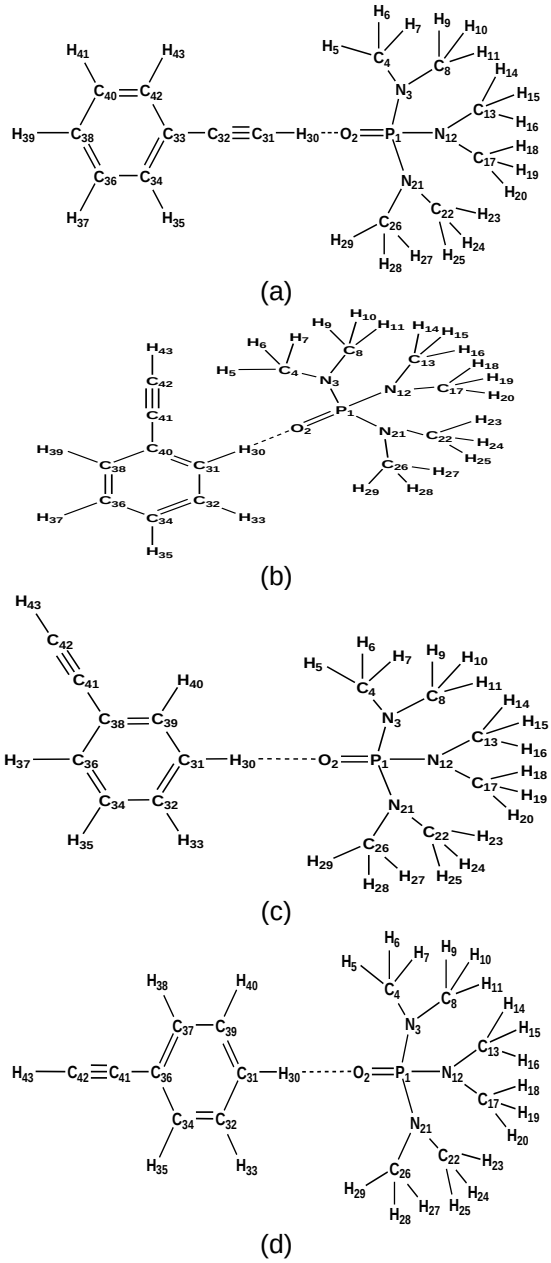

Fig 6. Molecular configuration of paired-molecule and H-acidic and oxygen distances between phenylacetylene and HMPT (a) linearly: r/Å=2.1408, ortho: r/ which =2.4200, meta: r/ which = -, para: r/A^o=2.3863.

this can only be happened for the linearly Ph-C≡CH...HMPA paired-molecule orientation.

Energy and geometry optimation of molecule

The result of calculation of energy and other parameters are included in Table 2. Ph-C≡CH... HMPA paired-molecule with linearly configuration had ΔE_k lower than others. So the linearly orientation, Fig 6(a),

conform to the T_1 relaxation time data of phenylacetylene in HMPA. These results are also confirm by the properties of single molecule, Fig 4(a).

CONCLUSION

In the HMPT solution non-degassed, the ^{13}C T_1 relaxation time of phenylacetylene was reduced four times. It means spectroscopycally that time measurement of ^{13}C NMR spectrum was also reduced.

In relation to the molecular mobility and its interaction, similarly with in the neat, rotational diffusion of phenylacetylene (pa) molecule in HMPA was anisotropic. Similarity ratio of ^{13}C T_1 relaxation time $C_{2,6}$ and $C_{3,5}$ with C_4 and C_8 in HMPT explains that the linearly interaction through H-acidic of HMPT and oxygen in HMPT was occurred.

Linearly shaped paired-molecule structure pa…HMPA was preferred than others shaped of paired-molecule configurations. This fact also confirmed by *ab initio* calculation.

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