A ROBUST EIGHT-MEMBERED RING MOTIF IN THE HYDROGEN-BONDED SUPRAMOLECULAR STRUCTURE OF DI(METHANE-SULFONYL)AMINE—PYRIDINE DERIVATIVES: SYNTHESIS AND CHARACTERIZATION.

ABSTRACT

The supramolecular structures of di(methanesulfonyl)amine—pyridine derivatives were synthesized by treating di(methanesulfonyl)amine equimolarly with 2,6-diaminopyridine and 2,6-dimethylpyridine, 2-(phenylamino)pyridine and 2-methylpyridine. The product were characterized by means of single crystal X-ray diffractometry, nuclear magnetic resonance spectroscopy and elemental analysis. Before characterizing the proposed supramolecular structures were designed by means of semi-empirical computational calculations, AM1. The calculation result was expected could give an adequate information on the possible motif of the hydrogen-bond of the designed structures.

Characterization results showed that the supramolecular structures of di(methanesulfonyl)amine—2,6-diaminopyridinium (monoclinic, Space group C2/c) adopted an antidromic double eight-membered ring $[R_2^2(8), R_2^2(8)]$ pattern as our prediction.

On the other hand, we have demonstrated a simple model for the construction of the antidromic ring motif $R_2^2(8)$ from 2-(phenylamino)-pyridinium-di(methanesulfonyl)amidate and 2,6-dimethylpyridinium-di(methane-sulfonyl)amidate (monoclinic, space group $P2_1/c$). However unfortunately we have failed to obtain good crystal of 2-methylpyridinium di(methanesulfonyl)-amidate which suitable for single crystal x-ray analysis.

The research result showed also that the computational calculation was not in qualitative agreement with the experimental research.

Karna Wijaya
Iqmal Tahir

Department of Chemistry, Faculty of Mathematics and Natural Sciences
Gadjah Mada University, Yogyakarta

I. INTRODUCTION

The concept and term of supramolecular chemistry were introduced in 1978 as a development and generalization of erlier work in which the seed had been planted [1,2,3] and over recent years, this supramolecular chemistry has developed rapidly. With the progress of supramolecular chemistry, there has been a concomittant shift in the mindset of chemist working in this field. As a consequence of this intense interest in this field, a very large number of synthetic supramolecular systems have now been synthesized, with many of the systems ranging in size from around a nanometer. This field remains an exciting and fast moving one that continous to produce a range of new materials. Much of the work in supramolecular chemistry has focused on molecular design for achieving complementarity between single molecule hosts and guests. As a consequence, the practice of supramolecular chemistry tends to be somewhat interdisplinary activity, often requiring knowledge of a range of appropriate chemical, physical and biochemical procedures and techniques [2,4,5].

Self-organization via hydrogen-bond may open up our perspectives in material chemistry towards an area of supramolecular materials whose features depend on molecular information. Supramolecular crystal engineering also gives access to the controlled generation of well-defined supramolecular architectures and patterns in molecular layers, films, membranes, micells, polymer etc [6,7,8,9,10]. Our current

research is intended to open new possibility in designing robust eight- membered ring supramolecular structures based on di(methanesulfonyl)amine and pyridine derivates compounds. In this research, we have tried to synthesize that eight membered ring supramolecular structures with pyridine derivates and di(methylsulfonyl)amine as building block. So far some researchers mostly use only monomolecule derivates of pyridine or pyrimidine to form eight-membered ring supramolecular structures. With this supramolecular research, we hope, we could understand, for instance, molecular recognition in biological systems, such as substrate binding to a receptor protein, enzyme reactions, assembly of protein-protein complexes, immunological antigen-antigen association, intermolecular reading of the genetic code, signal induction by neurotransmitters and cellular recognition [9,11,12,13].

II. RESEARCH METHODOLOGY

This work was divided into two sections. The first was computational prediction of the designed supramolecule structures and the second was synthesis of those structures.

II.1 Prediction of the Hydrogen-Bond Motif

The supramolecule structure prediction was performed by using licensed HYPERCHEM 6 package programmed which was available in AIC (Austrian-Indonesian Computer Centre)-GMU (Gadjah Mada University).

The supramolecule structures were optimized in its lowest energy state using the semi-empirical quantum chemical AM1 method available in the Hyperchem 5.0 package. The initial structure of the supramolecule structures were built using the software and mechanically optimized structures were converted into AM1 input file and were calculated by this AM1 calculation method.

II.2 Synthesis of derivate pyridine-di(methanesulfonyl)amine

Di(methanesulfonyl)amine has been synthesized by the main researcher during his research work in Technische Universitaet Braunschweig, Republic Federal Germany. The pyridine derivatives will be purchased

II.3 Synthesis of 2-methylpyridinium-di(methanesulfonyl)amidate

This compound was prepared by dissolving di(methanesulfonyl)amine (1,73 g, 10,0 mmol) and 2-methylpyridine (0,93 g, 10,0 mmol) in acetonitrile (5 ml). The solution was kept in low temperature (-30°C) until the product was crystallized. The product was then characterized by ^{1}H-NMR, elemental analysis and single crystal X-ray diffractometry.

II.4 Synthesis of 2-(phenylamino)pyridinium-dimethanesulfonylamidate

Similar procedure with above mentioned procedure (procedure a)

The used di(methanesulfonyl)amine	*0,52 g (3,0 mmol)*
The used 2-(phenylamino)pyridine	*0,51 g (3,0 mmol)*
Solvent	*Methanol (10 ml) or other suitable solvent such as Ethanol, etc*
Characterization	*^{1}H-NMR, elemental analysis and single crystal X-ray diffractometry*

II.5 Synthesis of 2,6-diaminopyridinium-di(methanesulfonyl)amidate

Similar procedure with above mentioned procedure (procedure a)

The used di(methanesulfonyl)amine	*1,72 g (10,0 mmol)*
The used 2,6-diaminopyridine	*1,09 g (10,0 mmol)*
Solvent	*Acetonitrile (10 ml) or other suitable solvent such as Ethanol, etc*
Characterization	*^{1}H-NMR, elemental analysis and single crystal X-ray Diffractometry*

II.6 Synthesis of 2,6-dimethylpyridiniumi-di(methanesulfonyl)amidate

Similar procedure with above mentioned procedure (procedure a).

The used di(methanesulfonyl)amine	*1.72 g (10.0 mmol)*
The used 2,6-dimethylpyridine	*1.07 g (10.0 mmol)*
Solvent	*Acetonitrile (10 ml) or other suitable solvent such as Ethanol, etc*
Characterization	*H-NMR, elemental analysis and single crystal X-ray diffractometry*

III. RESULTS AND DISCUSSION

III.1 Computationally Study

The goal of the study was to predict wheater an antidromic ring hydrogen bonded $R_2^1(8)$ can be designed from derivatives of pyridines and di(methanesulfonyl)amine. To gain the goal the four supramolecular structures (fig. 1,2,3,4) were fully optimized with molecular mechanic (mm) calculation. The optimized structures were then calculated with semi-empirical method, AM1. The computational study predicted that the both species from each structure prefered to hydrogen bond randomly. The hydrogen bridges deviated significantly from our prediction, ie formation of antidromic ring hydrogen bonded $R_2^1(8)$.

Fig. 1 Optimized geometries of 2-phenyl amino-pyridinium –dimethane sulfonylamidate

Fig. 2 Optimized geometries of 2-methylpyridiniumfomethane—sulfonylamidate

Fig. 3 Optimized geometries of 2,6-methyl pyridinium—dimethanesulfonylamidate

Fig. 4 Optimized geometries of 2,6 Diammonmethy pyridinium—dimethanesulfonyl amidate

III.2 Experimental Study

III.2.1 Synthesis of 2-methylpyridinium-di(methanesulfonyl)amidate

Unfortunately we could not grow a suitable single crystal for X-ray analysis, although the NMR (Nuclear Magnetic Resonance) and elemental analysis (CHNS analysis) were in agreement with the purposed structures. Therefore, in this report we could not show the structure.

III.2.2 Synthesis of 2-(phenylamino)pyridinium-dimethanesulfonylamidate

As stated above nowdays we are engaged in a systematic study of hydrogen-bond patterns in crystalline onium di(methanesulfonyl)amidates both experimentally and theoretically. The anion common of these compounds, $(MeSO_2)_2N$ adopts a fairly rigid solid-state conformation of pseudo C_2 symmetry, exhibiting two setereochemically different pairs of O atoms characterized by trans- and gauche-O-S-N-S torsions angles, respectively. Thus, three of its five potential hydrogen-bond acceptors are included in a nearly planar O-S-N-S-O sequence, which when combined with complementary cation donor species, provides a robust supramolecular synthon for constructing hydrogen-bonding patterns of tunable complexity. On the other hand, pyridine derivatives such as 2-(phenylamino)pyridine provide an electronegative nitrogen atom which is potential as an acceptor proton. With these two compounds one may design a robust eight-membered ring supramolecular structure of the 2-(phenylamino)pyridinium-di(methane-sulfonyl)amidate.

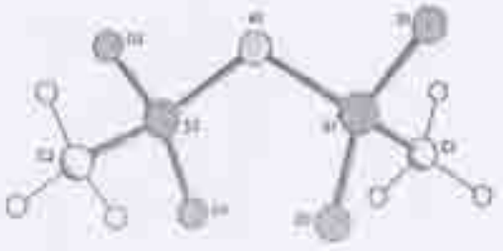

Fig.5. Anion of di(methanesulfonyl)amidate

The crystallographic data for 2-(phenylamino)pyridinium-di(methanesulfonyl)amidate are compiled in table 1. Table 2 contains the torsion angles of the di(methanesulfonyl)amidate anion structure as a proof for the konformative persistence of the anion.

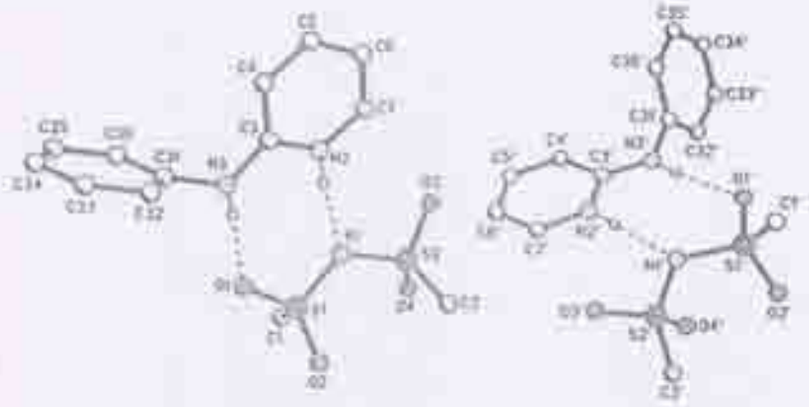

Fig. 6. Two independent ionpair with antidromic ring motif $R_2^2(8)$

Table 1. The crystallographic, NMR and elemental analysis data of 2-(phenylamino)pyridinium-di(methanesulfonyl)amidate

Empirical formula	$C_{14}H_{17}N_3O_4S_2$	
Formula weight	*343.42*	
Temperature	*143(2) K*	
Wavelength	*0.71073 A*	
Crystal system	*Triclinic*	
Space group	*P-1*	
Unit cell dimensions	*a = 8.394(2) A*	*α= 102.93(2)°*
	b = 10.780(3) A	*β= 93.03(2)°*
	c = 17.858(5) A	*γ = 90.32(2)°*
Volume	*1572.5(7) A^3*	
Z	*2*	
Density (calculated)	*1.451 Mg/m^3*	

Table 2. Torsionangle (°) of the di(methanesulfonyl)amidate-anion

O(1)-S(1)-N(1)-S(2)	176.7(2)	173.2(1)
O(2)-S(1)-N(1)-S(2)	48.9(2)	45.9(2)
C(1)-S(1)-N(1)-S(2)	-69.7(2)	-72.5(2)
O(3)-S(2)-N(1)-S(1)	172.4(1)	174.1(1)
O(4)-S(2)-N(1)-S(1)	44.9(2)	46.6(2)
C(2)-S(2)-N(1)-S(1)	-73.3(2)	-71.6(2)

The left coulmn is for the left structure of the compound

As stated above, The both species, i.e. 2-(phenylamino)-pyridinium and di(methanesulfonyl)amidate fulfill the requirements to form supramolecular structures. The crystals consist of ion pairs which the components are associated with each other via a N—H···N and a N—H···O hydrogen bond under formation of the antidromic ring motif $R_2^2(8)$. The supramolecular compound contains two independent, however geometrically similar ion pairs.

In the independent ion pairs of 2-(phenylamino)pyridinium-di(methanesulfonyl)amidate, the pyridinium cations are chemically unsymmetrical and capable to form supramolecule bonding isomerism. In the structure, we can demonstrate that two bridges connect the two species through N-H-Bridge which come from the pyridinium ring and the N-H bridges from the amino group.

The successful construction of the antidromic motif $R_2^2(8)$ require a recognition process and a good complementarity of the ionic elements. The di(methanesulfonyl)amidate-anion-*because of its geometrical persistence*- shows almost unchangeable acceptor distance N(1)···O(1) of approx. 240 pm, the complementary cations must, therefore, be adapted as good as possible to this value with regard to its intramolecule D···D [(N(2)···N(3)] distance.

For the cations in 2-(phenylamino)pyridinium-di(methanesulfonyl)amidate, N-C(3)-bonding length is observed ca 130 pm (which is correspondence with a strong partial double bond character, a sp^2 -hybridization) and the angle N(2)—C(3)—N(3) is approx. 120°.

The complex compatibility of the crystal package strengths causes significant differences in the relative orientation of the N(2)-C(3)-N(3) and N(1)-S(1)-O(1) planes so

that it may result more or less strong antidromic ring motif $R_2^2(8)$. However, the H-bridges are flexible enough to keep the robustness of the model.

III.2.3 Synthesis of 2,6-diaminopyridinium-di(methanesulfonyl)amidate and Synthesis of 2,6-dimethylpyridinium-di(methanesulfonyl)amidate

For the construction of a bicyclischen hydrogen bond pattern with two condensed $R_2^2(8)$-rings comes basically three possibilities into consideration (Fig. 7). The directionality of the rings depends on how the donor/acceptor interactions are distributed on the complementary molecular or Ionic components.

The synthesis of double ring models of kinds a) and b) was processed in recent years from numerous authors with most atractive success. However the double ring model of kind c) has paid a little attention. In this research, we present the crystall structures of two pyridinums, whose their cation-components would be expected to form antidromic ring motif type $[R_2^2(8), R_2^2(8)]$. The crystallographic, NMR and elemental a nalysis data of the two di(methanesulfony)amidate can be found in the table 3.

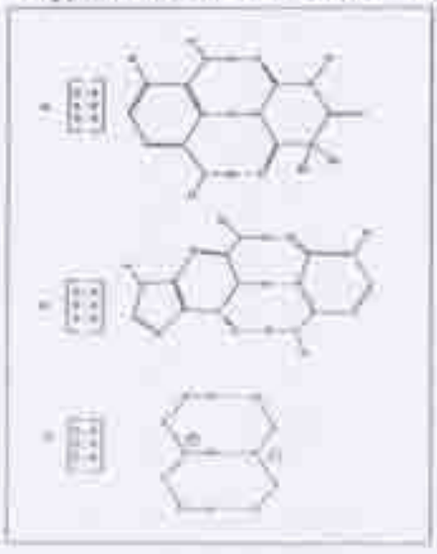

Fig. 7 Three possibilities to the construction of an antidromic ring motif $R_2^2(8)$ of Complementary molecular or Ionic components. (a) Two homodromic Rings, (b) an antidromic and a homodromic Rings and (c) Two antidromic Rings

Tab.3 The crystallographic, NMR and elemental analysis data of 2,6-diamino-pyridinium-di(methanesulfonyl)amidate and 2,6-dimethylpyridinium di(methanesulfonyl)amidate

	2,6-diaminopyridinium-di(methanesulfonyl)amidate	2,6-dimethylpyridinium-di(methanesulfonyl)amidate
formula	$C_5H_{11}N_3O_4S_2$	$C_9H_{15}N_2O_4S_2$
M_r	*282,34*	*280,36*
Crystall system	*Monoklin*	*Monoklin*
Space group	*C2/c*	*$P2_1/c$*
Lattice constant (pm $^{-1}$)		
a	*2053,9(5)*	*567,09(10)*
b	*1077,8(4)*	*2337,0(6)*

c	*1481.3(4)*	*998.7(3)*
α	*90*	*90*
β	*130.12(2)*	*101.76(3)*
γ	*90*	*90*
Z	*8*	*4*
^{1}H-NMR (60 MHz, CD_3CN/TMS	*δ = 2.99 (s, 6H, NCH_3), 6.50 (bs, 5H, NH) 5.93-5.96 und 7.44-7.52 (d/t, 3H, Har)*	*δ = 2.73 (s 6H, CCH_3), 2.90 (6H, SCH_3), 7.54-7.58 (d3H, Har)*
Yield	*2.34 g (90%)*	*2.52 g (90%)*
melting point	*162-164°C*	*90-95°C*
Elemental analysis Calculated (%) Found (%)	*C 29.76; H 5.00; N 19.64; S 22.71 C 30.11; H 4.96; N 19.64; S 22.38*	*C 38.56; H 5.75; N 9.99; S 22.87 C 38.49; H 5.74; N 9.96; S 23.03*

Asymmetric unit in the structure of 2,6-diaminopyridinium-di(methanesulfonyl)amidate was a ion pair with the expected $[R_2^2(8), R_2^2(8)]$-connectivity. In spite of optimal geometrical complementarity of the structure, the bicyclische system diverged quiet strong from the ideal markedness (Fig 8) with approximately coplanar [DDD]- and [AAA]-recognition (Fig 7, geometric data in Tab 4). The unique order of the ions was presumably due to the requirements of the remarkable two-dimensional H-bridge network, in which the ion pair were linked over that residual NH donors of the cation. The three H-bridges of the double ring model were considerably bent with approx. 160° and one of the lateral N-H...O-bridge was longer towards the expectation, on the other hand, the other one were shorter than the central N-H-Bond.

Fig. 8 Ion pair with twofold amidinium ring motif of $R_2^2(8)$ in crystal of 2,6-diaminopyridinium-di(methanesulfonyl)amidate

Tab. 4 The amidinium ring motif of $R_2^2(8)$ in 2,6-diaminopyridinium-di(methanesulfonyl)amidate: Bondlength, bondangle and nonbonded distance (pm, °).

N(2)—C(3)—N(7)	117,0(2)	N(2)—C(7)—N(4)	116,3(2)
N(2)—C(3)	135,5(3)	N(2)—C(7)	136,5(3)
N(3)—C(3)	134,1(3)	N(4)—C(7)	135,0(4)
N(2)···N(3)	229,9(3)	N(2)···N(4)	230,7(3)
H(01)—N(2)···C(3)	119(2)	H(01)—N(2)···C(7)	117(2)
H(02)—N(3)···C(3)	121(2)	H(04)—N(4)···C(7)	116(2)
N(1)—S(1)—O(1)	105,1(1)	N(1)—S(2)—O(3)	105,3(1)
N(1)—S(1)	160,0(2)	N(1)—S(2)	160,0(2)
O(1)—S(1)	144,2(2)	O(3)—S(2)	144,0(2)

N(1)···O(1)	241,8(3)	N(1)···O(3)	241,8(3)
N(2)—H(01)	79(3)		
H(01)···N(1)	221(3)		
N(2)···N(1)	297,1(3)		
N(2)—H(01)···N(1)	163(2)		
H(01)···N(1)—S(1)	133(1)	H(01)···N(1)—S(2)	106(1)
N(3)—H(02)	84(2)	N(4)—H(04)	82(2)
H(02)···O(1)	224(2)	H(04)···O(3)	310(2)
N(3)···O(1)	304,8(3)	N(4)···O(3)	287,9(3)
N(3)—H(02)···O(1)	164(3)	N(4)—H(04)···O(3)	158(3)
H(02)···O(1)—S(1)	108(1)	H(04)···O(3)—S(2)	134(1)

Naturally, the structure of 2,6-dimethylpyridinium-di(methanesulfonyl)-amidate was essentially lesser complex than that of 2,6-diaminopyridinium-di(methanesulfonyl)amidate. Because of the small load with H-bridges, the anion has an almost ideally C_2-symmetrical conformation. Cation and anion were associated through one comparative short and slightly bent $^+$N—H···N$^-$-hydrogen bond to the an ion pair (Fig. 8). The expected ring motif of $R_2^2(8)$ with two lateral C—H···O-interaction did not occur. The methyl substituent group $H_3C(31)$ was far away from the potential acceptor O(1). The distance between $H_3C(71)$ and O(3) was smaller and the C—H···O-interaction can be regarded — *in the frame of the accepted criteria* — as a weak H-bridge. Accordingly, a simple ring motif of $R_2^2(8)$ did not occur.

Tab. 5 The antidromic ring motif of $R_2^2(8)$ in 2,6-dimethylpyridinium-di(methanesulfonyl)amidate: Bondlength, Bondangle and nonbonded distance (pm, °)

N(2)···C(7)—C(71)	117,6(2)	N(2)—H(1)	82(2)
N(2)···C(7)	133,1(3)	H(1)···N(1)	199(2)
C(71)—C(7)	149,0(3)	N(2)···N(1)	280,5(3)
N(2)···C(71)	245,2(3)	N(2)—H(1)···N(1)	173(2)
H(1)···H(2)—C(7)	117(2)°	H(1)···N(1)—S(2)	118(1)
H(71C)—C(71)—C(7)	109,5		
N(1)—S(2)—O(3)	105,7(1)	C(71)—H(71C)	98
N(1)—S(2)	160,6(2)	H(71C)···O(3)	260
O(3)—S(2)	144,1(2)	C(71)···O(3)	328,5(3)
N(1)···O(3)	242,5(2)	C(71)—H(71C)···O(3)	128
		H(71C)···O(3)—S(2)	113

Tab. 6 The antidromic ring motif of $R_2^2(8)$ in 2,6-dimethylpyridinium-di(methanesulfonyl)-amidate : distance (pm) of the non hydrogen atoms of the middle plane of the atoms N(2), C(71), N(1) and O(3) (= middle D_2A_2-Plane)[a]

N(2)	67,1(1)	C(7)	49,8(3)
C(71)	-53,3(1)	S(2)	-45,4(2)
N(1)	-66,6(2)		
O(3)	52,7(1)		

[a] *Pseudotorsionsangel N(2)···N(1)···O(3)···C(71) : 41,4(1)°*

Tab. 7 C—H···O-Interaction in 2,6-dimethylpyridinium-di(methanesulfonyl)-amidate (distance in pm, angel in °) [a]

Nr.	D—H···A	D—H	H···A	D···A	angel
1	C(4)—H(4)···O(2')	95	258	330,3(3)	163
2	C(5)—H(5)···O(4")	95	234	328,0(3)	168
3	C(6)—H(6)···O(3")	95	255	348,6(3)	170
4	C(1)—H(1C)···O(2")	98	247	344,4(3)	170
5	C(2)—H(2C)···O(4')	98	230	319,7(3)	151

[a] *Symmetrioperator : (i) x, y, z + 1; (ii) x + 1, y, z + 1; (iii) x + 1, -y + 1.5, z + 0.5; (iv) -x, -y + 1, -z; (v) x + 1, y, z*

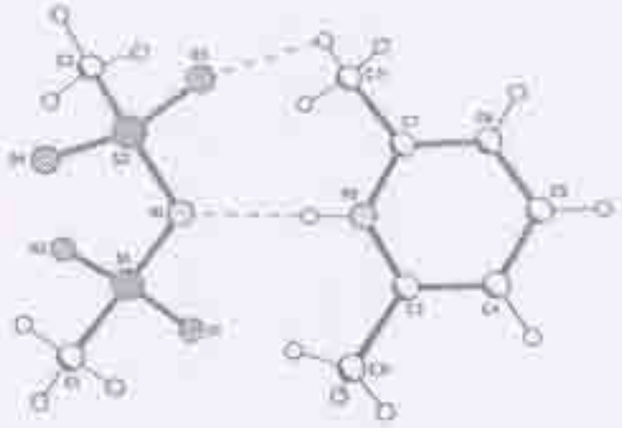

Fig.9 Ion pair in crystal von 2,6-dimethylpyridinium-di(methanesulfonyl)-amidate

The geometrical data of the antidromic ring motif of $R_2^2(8)$ are compiled in the Tab.5, 6 and 7. From the table, one recognizes that H···O-distance in the H-bridge was rather precise the sum of the van der Waals radii, meanwhile the angles C—H···O was circa 10° larger as the recommended cut off boundary of 120°

The order of the ion pairs at the crystal packing was embossed by five C—H···O-H-Bond, those went out from the aromatic CH groups of the cation and/or the activated methyl substituent groups of the anion and with H···O < 260 pm as well as C—H···O > 150° the bond were considerably more prominent as the presumed C—H···O within the ion pair (Tab 7).

Structure 2,6-dimethylpyridinium-di(methanesulfonyl)-amidate illustrates the principle, that C—H···O interaction will be occurred when a larger surplus of classical acceptors compared to classical donors is available (here: D-H/A = 1/5).

CHAPTER V

CONCLUSION

Characterization results showed that the supramolecular structures of di(methanesulfonyl)amine—2,6-diaminopyridinium (*monoclinic, Space group C2/c*) adopted an antidromic double eight-membered ring motif of $[R_2^2(8),R_2^2(8)]$ meanwhile

di(methanesulfonyl)amine—2,6-dimethylpyridinium (*monoclinic, space group* $P2_1/c$,) showed deviation from ring motif of $[R_2^2(8),R_2^2(8)]$.

In conclusion, we have demonstrated a simple model for the construction of the antidromic ring motif of $R_2^2(8)$ from (phenylamino)pyridinium di(methanesulfonyl)amidate (*Triclinic, P-1*). The results clearly demonstrate that these weak interactions are capable of not only constructing well-defined crystal structures but also antidromic ring motif $R_2^2(8)$. However unfortunately we have failed to obtain good crystal of 2-methylpyridinium di(methanesulfonyl)amidate which suitable for single crystal x-ray analysis.

The research result showed also that the computational calculation was not in qualitative agreement with both the experimental research and purposed structures.

REFERENCES

1. Lehn, J.M., 1995. Supramolecular Chemistry: Concepts and Perspectives. VCH: Weinheim.
2. Voegtle, F., 1992, Supramoleculare Chemie. Teubner Studienbuecher, Stuttgart.
3. Lindoy, L.F. and Atkinson, I.M., 2000. Self-Assembly in Supramolecular Systems, Royal Society of Chemistry, New South Wales.
4. Grant, G.H., 1995, Computational Chemistry, Oxford Science Publication, Oxford.
5. Desiraju, G.R., (1995), Angew Chem 107, 2541-2558.
6. Subramanian, S and Zaworotko, M.J. (1994), Coord. Chem. Rev. 137, 357-401.
7. Braga, D. and Grepioni, F., (1998), New J. Chem. 22, 1159-1161.
8. Wijaya, K., 1999, Dissertation, TU Braunschweig.
9. Allen, F.H., Motherwell, W.D.S., Raithby, P.R., Shields., G.P. and Taylor, R., (1999), New J. Chem. 23, 25-34.
10. Aakeröy, C.B. (1997), Acta Cryst. B53, 569-586.
11. Aakeröy, C.B. and Seddon, K.R., (1993), Chem.Soc. Rev., 22, 397-407.
12. Mascal, M., Fallon, P.S., Batsanov, A.S., Heywood, B.R., Champ, S., and Colclough, M., (1995), J.Chem.Soc.Chem.Commun., pp.805-806.
13. Subramanian, S and Zaworotko, M.J. (1994), Coord. Chem. Rev. 137, 357-401.

ACKNOWLEDGEMENT

We thank ITSF (Indonesia Toray Science Foundation) for the financial help and Technische Universitaet zu Braunschweig for the use of X-ray analytical facilities (Prof. Dr. P.G. Jones and Dr. Oliver Mours) and Dr.Anwar Usman for valuable X-ray discussion. Also we would like to thank AIC (Austria Indonesia Centre) for Computational Research facility, Faculty of mathematics and Natural Sciences, Gadjah Mada University for the computational calculation.