A ROBUST EIGHT–MEMBERED RING MOTIF IN THE HYDROGEN-BONDED STRUCTURE OF 2-(PHENYLAMINO)PYRIDINIUM- DI(METHANESULFONYL)AMIDATE

Karna Wijaya, Iqmal Tahir
Chemistry Department, Faculty of Mathematics and Natural Sciences
Gadjah Mada University, Yogyakarta

Armand Blaschette, Oliver Mours, Peter G. Jones
Institute fuer Analytische und Anorganische Chemie, Technische
Universitaet zu Braunschweig, Germany

ABSTRACT

The compound was prepared by dissolving 2-(phenylamino)pyridine (0.52 g ; 3.0 mmol) and di(methanesulfonyl)amine (0.51 g; 3.0 mmol) in 5 mL methanol. Slow partial evaporation of the solvent at low tempertaure (-30°C) gave a yield of 0.66 g (64%) and crystals suitable for X-ray study (m.p. 150-152°C). The single crystal X-ray result showed that the crystal system was trikline with space group P $\overline{1}$.

The crystal structure of the title compound 2-(phenylamino)pyridinium-di(methanesulfonyl)amidate forms a robust antidromic ring motif type $R_2^2(8)$. The structure testifies to the persistence of the $R_2^2(8)$ in question, which was previously detected as a robust supramolecular synthon in 2-aminopyridinium di(benzenesulfonyl)amidate and in a series of onium di(methane-sulfonyl)amidates.

Keywords: *supramolecule, hydrogen-bond*

INTRODUCTION

The design of supramolecular structure depends crucially on the robustness or high probability of formation, of a limited number of supramolecular synthons [1]. Among these non-covalent interactions, bimolecular hydrogen-bonded ring motifs [2] are prominently utilized for controlling the assembly of complementary molecular building blocks into finite or infinite architectures [3]. Since the hydrogen bond is primariliy electrostatic in nature, the strengths of such interactions involving charged species in enhanced and, as a result, acyclic or preferentially cyclic hydrogen-bonded motifs become a powerful tool for linking ions together in a predictable manner [4].

To prepare a crystal containing a supramolecular structure of interest, one must first identify molecular functionalities of the target molecules that will generate predictable intermolecular interactions. Among these molecules, Di(methanesulfonyl)amine and derivates of pyridine are potentially of great interest as supramolecular building block. The N-H, S=O of the di(methanesulfonyl)amine and nitrogen atom of the pyridine derivates would seem to be a useful hydrogen-bonding unit [5].

In the present research we have attempted to design new robust eight membered-ring hydrogen-bonded networks of di(methanesulfonyl)amine and derivates of pyridine *i.e.* 2-(phenylamino)pyridine with antidromic ring motif type $R_2^2(8)$.
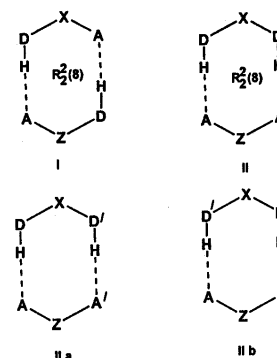

Fig.1 An eight- membered ring hydrogen-bonded network $R_2^2(8)$.

EXPERIMENTAL

The compound was prepared by dissolving 2-(phenylamino)pyridine (0.52 g ;3.0 mmol) and di(methanesulfonyl)amine (0.51 g; 3.0 mmol) in 5 mL methanol. Slow partial evaporation of the solvent at low temperature (-30°C) gave a yield of 0.66 g (64%) and crystals suitable for X-ray study.

RESULTS AND DISCUSSION

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, $(MeSO_2)_2N^-$, is derived from a strong N-H acid (pKa = 0.9, relative to water and 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.

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.
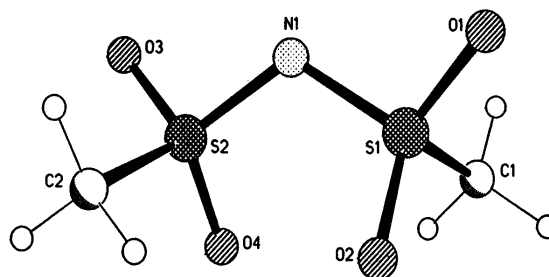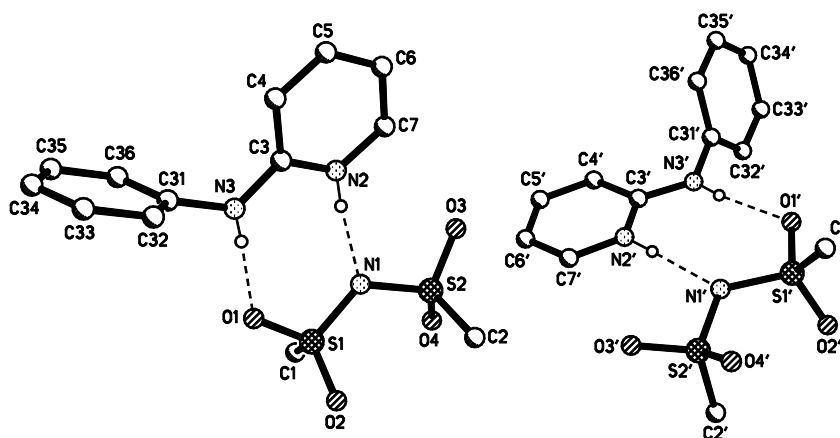

Fig.1. Anion of di(methanesulfonyl)amidate

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

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{13} H_{17} N_3 O_4 S_2$
Formula weight	343.42
Temperature	143(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.394(2) Å α= 102.93(2)°
	b = 10.780(3) Å β= 93.03(2)°
	c = 17.858(5) Å γ = 90.32(2)°
Volume	1572.5(7) Å^3
Z	4
Density (calculated)	1.451 Mg/m^3
Absorption coefficient	0.359 mm^{-1}
F(000)	720
Crystal size	0.75 x 0.46 x 0.23 mm^3
Theta range for data collection	3.08 to 27.55°
Index ranges	-10<=h<=10, 0<=k<=14, -23<=l<=22
Reflections collected	7577
Independent reflections	7200 [R(int) = 0.0161]
Completeness to theta = 27.55°	99.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7200 / 0 / 417
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1162
R indices (all data)	R1 = 0.0627, wR2 = 0.1288
Largest diff. peak and hole	0.643 and -0.535 e.Å^{-3}

Table 2. Torsions angle (^{o}) 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 column is for the left structure of the compound

As stated above, The both spesies, i.e 2-(phenylamino)-pyridinium and di(methane-sulfonyl)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 spesies 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 –hybridisation) 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.

CONCLUSION

In conclusion, we have demonstrated a simple model for the construction of the antidromic ring motif $R_2^2(8)$ from **-**(phenyl-amino)pyridine and di(methanesulfonyl)amine. The results clearly demonstrate that these weak interactions are capable of not only constructing well-defined crystal structures but also antidromic ring motif $R_2^2(8)$.

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APPENDICES

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	3227(2)	1688.1(18)	-1891.4(11)	23.5(4)
S(1)	2589.2(7)	972.4(5)	-2736.4(3)	27.2(1)
O(1)	3752(3)	1289(2)	-3234.3(11)	48.3(6)
O(2)	962(2)	1239.0(19)	-2913.4(12)	44.7(5)
C(1)	2701(3)	-675(2)	-2800.4(16)	33.2(5)
S(2)	2244.6(7)	1662.7(5)	-1147.6(3)	24.0(1)
O(3)	3290(2)	2251.6(18)	-500.4(10)	32.5(4)
O(4)	1641(2)	403.9(17)	-1152.5(11)	34.6(4)
C(2)	593(3)	2658(3)	-1167.1(17)	36.5(6)
N(2)	5766(2)	3520.5(19)	-1632.1(12)	25.7(4)
N(3)	6053(3)	3313(2)	-2930.1(12)	32.8(5)
C(3)	6492(3)	3889(2)	-2201.9(14)	24.9(5)
C(4)	7681(3)	4855(2)	-1989.9(14)	27.8(5)
C(5)	8058(3)	5351(2)	-1229.9(15)	29.8(5)
C(6)	7281(3)	4932(2)	-653.8(14)	29.7(5)
C(7)	6125(3)	4023(2)	-877.5(14)	27.1(5)
C(31)	6882(3)	3516(2)	-3574.8(14)	30.3(5)
C(32)	6454(4)	4499(3)	-3920.0(18)	46.5(7)
C(33)	7261(5)	4678(4)	-4547(2)	57.1(9)
C(34)	8458(4)	3883(4)	-4825.7(17)	52.2(9)
C(35)	8889(4)	2914(4)	-4472.2(19)	55.8(9)
C(36)	8097(4)	2725(3)	-3847.4(17)	45.4(7)
N(2')	1045(2)	1523.9(19)	1616.4(11)	23.8(4)
N(3')	1448(3)	1736(2)	2924.9(12)	30.0(5)
C(3')	1816(3)	1162(2)	2209.1(13)	23.6(5)
C(4')	2949(3)	182(2)	2036.1(14)	27.1(5)
C(5')	3225(3)	-327(2)	1286.9(15)	30.1(5)
C(6')	2401(3)	86(2)	683.0(14)	29.4(5)
C(7')	1305(3)	1002(2)	870.2(13)	26.4(5)
C(31')	2322(3)	1567(2)	3604.2(13)	25.9(5)
C(32')	1601(3)	940(3)	4096.6(16)	39.4(6)
C(33')	2418(4)	838(3)	4776.1(17)	46.9(7)
C(34')	3940(4)	1330(3)	4950.7(16)	44.0(7)
C(35')	4657(3)	1930(3)	4448.9(17)	44.9(7)
C(36')	3846(3)	2060(3)	3775.7(16)	37.1(6)
N(1')	-1455(2)	3333.3(18)	1919.7(11)	22.5(4)
S(1')	-2036.4(7)	3997.3(5)	2752.5(3)	24.1(1)
O(1')	-872(2)	3637.9(19)	3286.9(10)	39.0(5)
O(2')	-3679(2)	3703.3(18)	2846.6(11)	36.6(4)
C(1')	-1875(3)	5659(2)	2866.4(16)	35.4(6)
S(2')	-2520.3(7)	3358.2(5)	1150.1(3)	22.6(1)
O(3')	-1546(2)	2796.6(17)	528.1(10)	30.9(4)
O(4')	-3119(2)	4609.6(17)	1146.9(10)	33.6(4)
C(2')	-4183(3)	2332(3)	1110.8(15)	34.3(6)

Table 4. Bond lengths [Å] and angles [°].

N(1)-S(1)	1.596(2)	N(2')-C(3')	1.344(3)
N(1)-S(2)	1.605(2)	N(2')-C(7')	1.355(3)
S(1)-O(2)	1.431(2)	N(3')-C(3')	1.343(3)
S(1)-O(1)	1.443(2)	N(3')-C(31')	1.432(3)
S(1)-C(1)	1.757(3)	C(3')-C(4')	1.418(3)
S(2)-O(3)	1.4377(18)	C(4')-C(5')	1.360(3)
S(2)-O(4)	1.4438(18)	C(5')-C(6')	1.407(3)
S(2)-C(2)	1.762(3)	C(6')-C(7')	1.352(3)
N(2)-C(3)	1.345(3)	C(31')-C(36')	1.375(4)
N(2)-C(7)	1.352(3)	C(31')-C(32')	1.383(4)
N(3)-C(3)	1.341(3)	C(32')-C(33')	1.388(4)
N(3)-C(31)	1.433(3)	C(33')-C(34')	1.374(5)
C(3)-C(4)	1.412(3)	C(34')-C(35')	1.377(5)
C(4)-C(5)	1.362(4)	C(35')-C(36')	1.385(4)
C(5)-C(6)	1.401(3)	N(1')-S(1')	1.6021(19)
C(6)-C(7)	1.355(3)	N(1')-S(2')	1.6051(19)
C(31)-C(36)	1.371(4)	S(1')-O(2')	1.4395(19)
C(31)-C(32)	1.380(4)	S(1')-O(1')	1.4444(19)
C(32)-C(33)	1.387(4)	S(1')-C(1')	1.761(3)
C(33)-C(34)	1.365(5)	S(2')-O(3')	1.4387(18)
C(34)-C(35)	1.377(5)	S(2')-O(4')	1.4434(18)
C(35)-C(36)	1.381(5)	S(2')-C(2')	1.765(3)

S(1)-N(1)-S(2)	121.87(12)	C(3')-N(2')-C(7')	123.2(2)
O(2)-S(1)-O(1)	116.46(14)	C(3')-N(3')-C(31')	123.5(2)
O(2)-S(1)-N(1)	113.37(12)	N(3')-C(3')-N(2')	118.0(2)
O(1)-S(1)-N(1)	104.47(11)	N(3')-C(3')-C(4')	124.3(2)
O(2)-S(1)-C(1)	107.12(13)	N(2')-C(3')-C(4')	117.7(2)
O(1)-S(1)-C(1)	106.90(13)	C(5')-C(4')-C(3')	118.9(2)
N(1)-S(1)-C(1)	108.12(12)	C(4')-C(5')-C(6')	121.6(2)
O(3)-S(2)-O(4)	116.43(11)	C(7')-C(6')-C(5')	117.7(2)
O(3)-S(2)-N(1)	105.17(10)	C(6')-C(7')-N(2')	120.8(2)
O(4)-S(2)-N(1)	112.19(11)	C(36')-C(31')-C(32')	120.5(2)
O(3)-S(2)-C(2)	107.51(13)	C(36')-C(31')-N(3')	120.1(2)
O(4)-S(2)-C(2)	107.65(13)	C(32')-C(31')-N(3')	119.4(2)
N(1)-S(2)-C(2)	107.49(12)	C(31')-C(32')-C(33')	119.4(3)
C(3)-N(2)-C(7)	123.3(2)	C(34')-C(33')-C(32')	120.4(3)
C(3)-N(3)-C(31)	122.6(2)	C(33')-C(34')-C(35')	119.8(3)
N(3)-C(3)-N(2)	118.1(2)	C(34')-C(35')-C(36')	120.5(3)
N(3)-C(3)-C(4)	124.4(2)	C(31')-C(36')-C(35')	119.5(3)
N(2)-C(3)-C(4)	117.5(2)	S(1')-N(1')-S(2')	121.36(12)
C(5)-C(4)-C(3)	119.3(2)	O(2')-S(1')-O(1')	116.32(12)
C(4)-C(5)-C(6)	121.4(2)	O(2')-S(1')-N(1')	112.75(11)
C(7)-C(6)-C(5)	117.7(2)	O(1')-S(1')-N(1')	104.61(10)
N(2)-C(7)-C(6)	120.8(2)	O(2')-S(1')-C(1')	107.12(12)
C(36)-C(31)-C(32)	120.3(3)	O(1')-S(1')-C(1')	107.36(13)
C(36)-C(31)-N(3)	119.6(3)	N(1')-S(1')-C(1')	108.36(12)
C(32)-C(31)-N(3)	120.1(2)	O(3')-S(2')-O(4')	116.42(11)
C(31)-C(32)-C(33)	119.4(3)	O(3')-S(2')-N(1')	105.14(10)
C(34)-C(33)-C(32)	120.5(3)	O(4')-S(2')-N(1')	112.28(11)
C(33)-C(34)-C(35)	119.7(3)	O(3')-S(2')-C(2')	107.33(12)
C(34)-C(35)-C(36)	120.4(3)	O(4')-S(2')-C(2')	107.50(13)
C(31)-C(36)-C(35)	119.6(3)	N(1')-S(2')-C(2')	107.78(12)