Synthesis of *ortho*-sulfamidotriazobenzenes from 1,1'-Sulfonylbis(benzotriazole)

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SUPPORTING INFORMATION

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Melting points are uncorrected. NMR spectra were recorded in CDCl_3 with trimethylsilane as internal standard for ^1H (300 MHz) or solvent as the internal standard for ^{13}C (75 MHz). Microanalyses were performed on an elemental analyzer. Column chromatography was performed on silica gel 200–245 mesh.

Procedure for the preparation of 1. To 1-trimethylsilyl-1*H*-benzotriazole (5g, 26.2 mmol) in toluene (5 ml) at 0 °C was added dropwise sulfuryl chloride (1.77 g, 13.1 mmol) under nitrogen (Schlenk flask). The reaction mixture was stirred for 24 h warming to RT. The precipitate was filtered off and washed with diethyl ether to give 1, 1'-sulfonylbis-1*H*-benzotriazole (3.8g, 97%). The product is stable at RT for 24 h.

1,1'-Sulfonylbis(benzotriazole) 1. white crystal (97%); mp 165–166 °C (dec.) (lit. mp 130 °C);²¹ ^1H NMR (CDCl_3) δ 8.23 (d, J = 8.5 Hz, 2H), 8.09 (d, J = 8.2 Hz, 2H), 7.80–7.75 (m, 2H), 7.58–7.53 (m, 2H); ^{13}C NMR (CDCl_3) δ 145.2, 136.7, 131.6, 126.9, 121.0, 112.3. Anal. Calcd for $\text{C}_{12}\text{H}_8\text{N}_6\text{O}_2\text{S}$: C, 48.00; H, 2.69; N, 27.99. Found: C, 47.62; H, 2.52; N, 28.05.

Crystal data for 1: $\text{C}_{12}\text{H}_8\text{N}_6\text{O}_2\text{S}$, MW 300.00, monoclinic, space group C2/c , a = 20.8895(9), b = 5.2252(2), c = 14.8559(6) Å, β = 131.117(2)°, V = 1221.62(9) Å³, $F(000)$ = 616, Z = 4, T = -170 °C, μ (MoK α) = 0.281 mm⁻¹, D_{calcd} = 1.633 g.cm⁻³, $2\theta_{\text{max}}$ 50 ° (CCD area detector, MoK α radiation), GOF = 1.04, $wR(F^2)$ = 0.068 (all 3459 data), R = 0.026 (3253 data with $I > 2\sigma I$).

ORTEP diagram of 1,1'-sulfonylbis(benzotriazole) (Bt_2SO_2 , **1**)

ORTEP diagram of (*E*)-*N*-(2-(pyrrolidin-1-yl)diazenyl)phenylpyrrolidine-1-sulfonamide **2a**

Procedure for the preparation of 4a–c: The tube with 1-(morpholine-4-sulfonyl)-1*H*-benzotriazole (0.175 g, 0.65 mmol) and amine (0.11g, 1.3 mmol) was exposed to microwave irradiation (120 W) for 10 min at a temperature of 120 °C. After cooling to room temperature, the reaction mixture was purified by column chromatography on silica gel using 5–20% ethyl acetate in hexanes to give the unsymmetrical sulfamide **4a–c**.

4-(Pyrrolidine-1-sulfonyl)morpholine (4a): white crystal (90%); mp 53–54 °C (hexanes), ¹H NMR (CDCl₃) δ 3.77 (t, *J* = 4.7 Hz, 4H), 3.37 (t, *J* = 6.7 Hz, 4H), 3.25 (t, *J* = 4.9 Hz, 4H), 1.96 (quintet, *J* = 3.7 Hz, 4H); ¹³C NMR (CDCl₃) δ 103.3, 66.3, 48.5, 46.2, 25.6. Anal. Calcd for C₈H₁₆N₂O₃S: C, 43.62; H, 7.32; N, 12.72. Found: C, 44.00; H, 7.39; N, 12.58.

4-(Piperidine-1-sulfonyl)morpholine (4b): white crystal (88%); mp 70–72 °C (hexanes) (lit.²⁶ mp 71 – 72 °C); ¹H NMR (CDCl₃) δ 3.77 (t, *J* = 4.7 Hz, 4H), 3.25 (q, *J* = 9.5, 5.0 Hz, 8H), 1.65 (t, *J* = 6.8 Hz, 6H); ¹³C NMR (CDCl₃) δ 66.4, 47.3, 46.4, 25.5, 23.6. Anal. Calcd for C₉H₁₈N₂O₃S: C, 46.13; H, 7.74; N, 11.96. Found: C, 46.51; H, 7.83; N, 12.02.

4-(4-Methylpiperazine-1-sulfonyl)morpholine (4c): yellow oil²⁷ (80%); ¹H NMR (CDCl₃) δ 3.77 (t, *J* = 4.7 Hz, 4H), 3.38 (t, *J* = 4.9 Hz, 4H), 3.28 (t, *J* = 4.8 Hz, 4H), 2.54 (t, *J* = 4.9 Hz, 4H), 2.38 (s, 3H); ¹³C NMR (CDCl₃) δ 66.3, 54.3, 46.5, 46.2, 45.8.

EAGER 200 Stripchart

Sample Ident. : 11 1513(1a) Filename : 184711
 Analysed : 02-08-06 11:17:00 Printed : 02-08-2006 11:27:01

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV):-26.8
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 02-08-06 11:17:00 Printed : 02-08-2006 11:27:02
 Sample Ident. : 11 1513(1a) Filename : 184711
 Sample Weight : 2.11 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	73	141	121	5677.7	151362	14.15	Nitrogen
2	FU	141	345	163	25620.8	799942	74.80	Carbon
3	RS	345	597	367	1942.8	118199	11.05	Hydrogen
						1069503	100.00	

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV):-26.8
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 02-08-06 11:17:00 Printed : 02-08-2006 11:27:02
 Sample Ident. : 11 1513(1a) Filename : 184711
 Sample Weight : 2.11 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	121	151362	28.045	.528497E+01	Nitrogen
2	163	799942	47.617	.100000E+01	Carbon
3	367	118199	2.519	.676776E+01	Hydrogen

EAGER 200 Stripchart

Sample Ident. : 10 LK555 Filename : 196810
 Analysed : 12-04-06 10:47:56 Printed : 12-04-2006 10:57:59

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV): 18.4
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-04-06 10:47:56 Printed : 12-04-2006 10:57:59
 Sample Ident. : 10 LK555 Filename : 196810
 Sample Weight : 2.173 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	115	93	6961.9	120755	9.76	Nitrogen
2	FU	115	287	129	41555.3	814674	65.83	Carbon
3	RS	287	598	311	6965.9	302154	24.41	Hydrogen

1237583 100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV): 18.4
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-04-06 10:47:56 Printed : 12-04-2006 10:57:59
 Sample Ident. : 10 LK555 Filename : 196810
 Sample Weight : 2.173 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	93	120755	21.449	.674650E+01	Nitrogen
2	129	814674	52.166	.100000E+01	Carbon
3	311	302154	6.582	.269622E+01	Hydrogen

EAGER 200 Stripchart

Sample Ident. : 20 LK778 Filename : 197120
 Analysed : 12-11-06 12:31:14 Printed : 12-11-2006 13:39:28

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV): 2.3
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-11-06 12:31:14 Printed : 12-11-2006 13:39:29
 Sample Ident. : 20 LK778 Filename : 197120
 Sample Weight : 2.125 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	119	97	5796.6	107200	8.60	Nitrogen
2	FU	119	294	132	40264.0	817613	65.58	Carbon
3	RS	294	598	322	6761.9	321910	25.82	Hydrogen
							1246723	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV): 2.3
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-11-06 12:31:14 Printed : 12-11-2006 13:39:29
 Sample Ident. : 20 LK778 Filename : 197120
 Sample Weight : 2.125 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	97	107200	19.752	.762701E+01	Nitrogen
2	132	817613	54.645	.100000E+01	Carbon
3	322	321910	7.269	.253988E+01	Hydrogen

EAGER 200 Stripchart

Sample Ident. : 31 LK577 Filename : 197031
 Analysed : 12-08-06 14:47:15 Printed : 12-08-2006 14:57:18

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV): 1.4
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-08-06 14:47:15 Printed : 12-08-2006 14:57:18
 Sample Ident. : 31 LK577 Filename : 197031
 Sample Weight : 2.108 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	120	98	5658.9	107960	9.80	Nitrogen
2	FU	120	300	134	34795.9	724073	65.74	Carbon
3	RS	300	598	323	5943.7	269322	24.45	Hydrogen
							1101355	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV): 1.4
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-08-06 14:47:15 Printed : 12-08-2006 14:57:18
 Sample Ident. : 31 LK577 Filename : 197031
 Sample Weight : 2.108 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	98	107960	19.673	.670689E+01	Nitrogen
2	134	724073	47.576	.100000E+01	Carbon
3	323	269322	5.999	.268850E+01	Hydrogen

EAGER 200 Stripchart

Sample Ident. : 19 LK779 Filename : 197119
 Analysed : 12-11-06 12:21:11 Printed : 12-11-2006 13:39:26

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV): 9.4
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-11-06 12:21:11 Printed : 12-11-2006 13:39:27
 Sample Ident. : 19 LK779 Filename : 197119
 Sample Weight : 2.101 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	119	97	6150.1	114335	9.39	Nitrogen
2	FU	119	294	133	37687.8	762025	62.60	Carbon
3	RS	294	598	325	6828.7	340992	28.01	Hydrogen
							1217353	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV): 9.4
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 12-11-06 12:21:11 Printed : 12-11-2006 13:39:27
 Sample Ident. : 19 LK779 Filename : 197119
 Sample Weight : 2.101 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	97	114335	21.308	.666484E+01	Nitrogen
2	133	762025	51.512	.100000E+01	Carbon
3	325	340992	7.788	.223473E+01	Hydrogen

EAGER 200 Stripchart

Sample Ident. : 17 LK66 Filename : 180917
 Analysed : 11-04-05 12:04:54 Printed : 11-04-2005 12:14:56

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV):-5.5
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 11-04-05 12:04:54 Printed : 11-04-2005 12:14:57
 Sample Ident. : 17 LK66 Filename : 180917
 Sample Weight : 2.135 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	67	134	112	5095.5	118746	10.08	Nitrogen
2	FU	134	317	152	32005.5	807569	68.53	Carbon
3	RS	317	598	346	4796.4	252170	21.40	Hydrogen

1178485 100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV):-5.5
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 11-04-05 12:04:54 Printed : 11-04-2005 12:14:57
 Sample Ident. : 17 LK66 Filename : 180917
 Sample Weight : 2.135 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	112	118746	21.025	.680082E+01	Nitrogen
2	152	807569	49.666	.100000E+01	Carbon
3	346	252170	5.274	.320248E+01	Hydrogen

EAGER 200 Stripchart

Sample Ident. : 16 LK51 Filename : 180116
 Analysed : 10-17-05 10:00:07 Printed : 10-17-2005 10:10:09

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV):-6.2
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 10-17-05 10:00:07 Printed : 10-17-2005 10:10:10
 Sample Ident. : 16 LK51 Filename : 180116
 Sample Weight : 2.126 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	67	134	113	4981.5	117099	11.01	Nitrogen
2	FU	134	319	153	28779.1	735572	69.17	Carbon
3	RS	319	598	341	4313.9	210705	19.81	Hydrogen
							1063376	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV):-6.2
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 10-17-05 10:00:07 Printed : 10-17-2005 10:10:10
 Sample Ident. : 16 LK51 Filename : 180116
 Sample Weight : 2.126 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	113	117099	20.813	.628162E+01	Nitrogen
2	153	735572	45.150	.100000E+01	Carbon
3	341	210705	4.449	.349101E+01	Hydrogen

INDEX	FREQUENCY	PPM	HEIGHT
1	2432.416	8.106	13.0
2	2425.411	8.083	13.6
3	2424.038	8.078	12.5
4	2271.582	7.570	11.9
5	2264.440	7.547	16.0
6	2236.971	7.455	16.3
7	2235.598	7.450	16.0
8	2231.065	7.435	15.7
9	2229.554	7.430	20.2
10	2227.631	7.424	13.4
11	2223.099	7.409	11.9
12	2221.726	7.404	12.1
13	2179.972	7.265	25.8
14	2177.362	7.256	37.4
15	2175.714	7.251	37.7
16	2172.693	7.241	18.3
17	2172.006	7.238	18.3
18	2170.785	7.233	24.7
19	2134.785	7.114	22.7
20	2133.137	7.109	24.5
21	2131.076	7.102	12.4
22	2129.566	7.097	13.1
23	2127.643	7.091	14.0
24	2125.033	7.082	15.1
25	1077.487	3.591	151.2
26	-0.000	-0.000	19.3

EAGER 200 Stripchart

Sample Ident. : 11 LK 110 Filename : 183911
 Analysed : 01-17-06 11:43:05 Printed : 01-17-2006 13:30:44

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV):-0.8
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 01-17-06 11:43:05 Printed : 01-17-2006 13:30:44
 Sample Ident. : 11 LK 110 Filename : 183911
 Sample Weight : 2.151 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	73	143	125	3892.7	105132	8.66	Nitrogen
2	FU	143	336	166	28058.1	912220	75.17	Carbon
3	RS	336	598	360	3475.1	196215	16.17	Hydrogen
							1213567	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV):-0.8
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 01-17-06 11:43:05 Printed : 01-17-2006 13:30:44
 Sample Ident. : 11 LK 110 Filename : 183911
 Sample Weight : 2.151 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	125	105132	19.817	.867690E+01	Nitrogen
2	166	912220	54.071	.100000E+01	Carbon
3	360	196215	4.046	.464909E+01	Hydrogen

INDEX	FREQUENCY	PPM	HEIGHT
1	10918.298	144.707	4.0
2	10469.396	138.757	12.1
3	10364.041	137.361	9.2
4	10011.332	132.686	3.8
5	9821.235	130.167	49.9
6	9781.154	129.636	12.8
7	9651.751	127.920	53.1
8	9457.647	125.348	12.6
9	9055.123	120.013	13.6
10	8480.253	112.394	13.5
11	5841.805	77.425	13.4
12	5809.740	77.000	14.3
13	5777.676	76.575	14.0
14	1561.610	20.965	17.3

INDEX	FREQUENCY	PPM	HEIGHT
1	1136.786	3.768	12.4
2	1132.116	3.773	17.2
3	1127.446	3.757	16.1
4	1020.590	3.401	7.7
5	1013.860	3.379	20.1
6	1007.130	3.356	10.0
7	981.858	3.272	13.9
8	976.914	3.256	17.6
9	972.301	3.241	14.6
10	596.051	1.986	7.8
11	592.342	1.974	9.5
12	589.321	1.964	19.7
13	586.299	1.954	11.0
14	582.591	1.942	9.1
15	10.815	0.036	6.7

¹H NMR of 4a

EAGER 200 Stripchart

Sample Ident. : 24 KL198 Filename : 200724
 Analysed : 02-28-07 13:19:17 Printed : 02-28-2007 15:30:24

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV): 4.8
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 02-28-07 13:19:17 Printed : 02-28-2007 15:30:24
 Sample Ident. : 24 KL198 Filename : 200724
 Sample Weight : 2.131 Calc.method: using 'K. Factors'

No. (#)	Type	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	63	115	95	3742.8	66092	6.41	Nitrogen
2	FU	115	284	129	33861.7	643987	62.42	Carbon
3	RS	284	597	316	6097.3	321634	31.17	Hydrogen
						1031713	100.00	

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV): 4.8
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 02-28-07 13:19:17 Printed : 02-28-2007 15:30:24
 Sample Ident. : 24 KL198 Filename : 200724
 Sample Weight : 2.131 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	95	66092	12.582	.974380E+01	Nitrogen
2	129	643987	44.006	.100000E+01	Carbon
3	316	321634	7.391	.200223E+01	Hydrogen

EAGER 200 Stripchart

Sample Ident. : 16 LK69 Filename : 180916
 Analysed : 11-04-05 11:54:52 Printed : 11-04-2005 13:26:24

EAGER 200 Peak Integration Report

Instrument name : Instrument #1 Bline drift (fV):-1.6
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 11-04-05 11:54:52 Printed : 11-04-2005 13:26:25
 Sample Ident. : 16 LK69 Filename : 180916
 Sample Weight : 2.097 Calc.method: using 'K. Factors'

No. (#)	Type (#)	Start (Sec)	End (Sec)	Ret Time (Sec)	Height (fV)	Area (fV*Sec)	Area % (%)	Name
1	FU	65	132	112	2952.6	66975	5.69	Nitrogen
2	FU	132	314	151	30218.8	742910	63.07	Carbon
3	RS	314	598	364	5387.7	367948	31.24	Hydrogen
							1177834	100.00

EAGER 200 Unk Report

Instrument name : Instrument #1 Bline drift (fV):-1.6
 Company Name : U of Florida Operator Ident. : KOU
 Analysed : 11-04-05 11:54:52 Printed : 11-04-2005 13:26:25
 Sample Ident. : 16 LK69 Filename : 180916
 Sample Weight : 2.097 Calc.method: using 'K. Factors'

Pk. (#)	Ret Time (Sec)	Area (fV*Sec)	Element % (%)	Area Ratio	Name
1	112	66975	12.074	.110923E+02	Nitrogen
2	151	742910	46.517	.100000E+01	Carbon
3	364	367948	7.835	.201906E+01	Hydrogen

KJ48PX	FREQUENCY	PPM	HEIGHT
1	1132.142	3.788	16.7
2	1127.197	3.773	19.0
3	1017.182	3.390	17.2
4	1012.238	3.373	14.5
5	1007.293	3.357	17.3
6	989.438	3.297	14.9
7	984.631	3.281	19.5
8	979.961	3.266	20.4
9	763.915	2.546	15.9
10	759.107	2.530	14.7
11	754.163	2.513	17.0
12	714.607	2.382	12.5
13			50.0