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N″-SULPHONYLFORMAMIDRAZONES; PREPARATION AND CHARACTERISATION

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Abstract—N″-Sulphonylformamidrazones have been prepared in good yields from the reaction between N-sulphonylformimidates and di- or tri-substituted hydrazines.

The actual tautomeric form present has been shown to be a hydrazide imide by ^{13}C NMR spectroscopy. ^{1}H and ^{13}C NMR spectra showed the existence of a *cis* and a *trans* isomer in solution, arising from hindered rotation around the CN^{1} bond.

In connection with our investigation on the structure of nitrogen containing compounds with the possibility of tautomerism such as N-sulphonylformamidines[1] and formamidrazones[2] we were interested in the hitherto unknown N″-sulphonylformamidrazones. For some formamidrazones the structure has been shown to be the *Z*-isomer of the amide hydrazone form $RNHCHNNR^{1}R^{2}$ by means of IR[3] and NMR[2,4] measurements. It was of interest to investigate the influence of the sulfonyl group on the position of the CN-double bond and on the number of isomers present in solution.

This paper reports the reaction between some N-sulphonylformimidates and di- or trisubstituted hydrazines to form N″-sulphonylformamidrazones and a discussion of the structure of the prepared compounds by means of IR, ^{1}H NMR and ^{13}C NMR measurements.

$$R^{1}SO_{2}NCHOEt + R^{2}NHNR^{3}R^{4} \rightarrow R^{1}SO_{2}NCHNR^{2}NR^{3}R^{4}$$

1a–k

Compound	R^1	R^2	R^3	R^4
1a	Me	H	Me	Me
1b	Ph	H	Me	Me
1c	*p*-$CH_3C_6H_4$	H	Me	Me
1d	Me	H	Et	Et
1e	*p*-$CH_3C_6H_4$	H	Et	Et
1f	Ph	H	Me	Ph
1g	*p*-$CH_3C_6H_4$	H	Me	Ph
1h	Me	Me	Me	Me
1i	Ph	Me	Me	Me
1j	*p*-$CH_3C_6H_4$	Me	Me	Me
1k	Ph	Me	Me	Ph

Scheme 1.

RESULTS

The synthesis of N″-sulphonylformamidrazones (**1**) proceeds easily on stirring equimolar amounts of N-sulphonylformimidate and substituted hydrazine in dry ether for a short period, giving yields of **1** from 20–85%.

The preparation of **2** was carried out by tosylation of N,N′-dimethyl-N-phenylformamidrazone, as the usual procedure[5] for preparation of this type of compounds did not give the desired product. Further details on the tosylation of amidrazones will be publisher later.

$$CH_3NCHNHN(CH_3)C_6H_5 + p\text{-}CH_3C_6H_4SO_2Cl \rightarrow p\text{-}CH_3C_6H_4SO_2NCH_3CHNN(CH_3)C_6H_5$$

2

To clarify which of the two tautomers (**A** or **B**) was present in solution, the ^{13}C NMR spectra of compounds **1a–g** with the possibility of tautomerism, were compared with the spectra of compounds **1h–k** and **2** with fixed position of the CN double bond (Table 1).

$$R^{1}SO_{2}NH{-}CH{=}N{-}NR^{3}R^{4}$$

A

$$R^{1}SO_{2}N{=}CH{-}NHNR^{3}R^{4}$$

B

As found for N-sulphonylformamidines[1] and formamidrazones[2] the ^{13}C NMR spectra were of great value for the discrimination between the two tautomers. The chemical shift values of the imino carbon atom for compound **1a–g** and for the model compounds **1h–k** were found in the region δ 153.7–162.8 while the imino carbon atom in the model for tautomer **A** was found at δ 130.2, thus strongly indicating the position of the CN double bond to be in conjugation with the sulphonylgroup as in tautomer **B**.

The IR spectra of the compounds were of no value in determining the tautomer present as the position of the CN stretching vibrations[6] for both tautomer **A** and tautomer **B** models were found in the region 1595–1605 cm^{-1}, while for the compounds with tautomeric possibility the CN-stretching/NH-bending vibrations were found in the region 1598–1655 cm^{-1}, probably coupled vibrations. The use of N-deuterated compounds did not give conclusive evidence regarding the actual tautomer either.

From Table 1 it can be seen that compounds **1a–g** show two sets of signals for the imino C atoms and for some or all of the other C atoms, it further appears that the number of signals depends on the solvent. For some compounds there is one set of signals for ring C atoms in DMSO-d_6 solution while there are two sets of signals in

Table 1. ^{13}C NMR chemical shift values (DMSO-d_6)

Compound		N-CH-N	Quaternary ring C-atoms in the $R-SO_2$-group C(1)	C(4)	Quaternary ring C-atoms in the N-Ph-group	Tertiary ring C-atoms[a] $R-SO_2$-group ortho	meta	para	N-Ph group ortho	meta	para	CH_3SO_2	$-NCH_2$	$-NCH_3N$
$CH_3SO_2NCH_2NCH_3(CH_3)_2$	1a	160.4 153.7										41.6	47.8 45.6	
$C_6H_5SO_2NCH_2NCH_3(CH_3)_2$	1b	160.4 153.8	142.5			125.9	128.9	131.8[b]					47.8 45.6	
$p-CH_3C_6H_4SO_2NCH_2NCH_3(CH_3)_2$	1c[c]	160.2 153.7	142.0	139.7		126.0	129.3[b]						47.9 45.6	
$CH_3SO_2NCH_2NCH_3(C_2H_5)_2$	1d	161.9 156.3										43.0 41.6	51.4 12.0 50.0 11.5	
$p-CH_3C_6H_4SO_2NCH_2NCH_3(C_2H_5)_2$	1e[c]	161.9 156.6	142.2 139.8			125.8	129.6[b]						51.4 12.1 50.1 11.5	
$C_6H_5SO_2NCH_2NCH_3(CH_3)C_6H_5$	1f	163.2 157.1	142.6 142.3		150.1 148.2	126.1 125.9	129.1 128.9	132.1 131.9	114.5 113.0	129.1 128.9	121.0 119.6		43.0 39.6	
$p-CH_3C_6H_4SO_2NCH_2NCH_3(CH_3)C_6H_5$	1g[c]	163.1 156.9	142.4 142.1	139.5 139.1	150.2 148.2	126.2 126.0	129.5 129.3		114.4 113.0	129.1 128.9	121.0 119.5		43.0 39.6	
$CH_3SO_2NCH_2NCH_3H(CH_3)_2$	1h	160.7										41.8	43.5	24.8
$C_6H_5SO_2NCH_2NCH_3H(CH_3)_2$	1i	160.2	142.4			126.0	128.9	131.9					43.5	25.0
$p-CH_3C_6H_4SO_2NCH_2NCH_3H(CH_3)_2$	1j[c]	160.1	142.1	139.5		126.1	129.4						43.5	25.0
$C_6H_5SO_2NCH_2NCH_3H(CH_3)C_6H_5$	1k	162.8 162.4 160.5 160.3	141.9 142.2		147.1 145.6	126.3	129.4	132.3	114.0 112.4	129.4 129.0	121.3 119.4		38.8	30.1
$p-CH_3C_6H_4SO_2N(CH_3)CH_2N(CH_3)C_6H_5$	2[c,d]	130.2	144.4	133.6	147.8	126.9	130.2		113.7	128.9	119.1		34.4	

[a] Assigned by means of spectra of model compounds. [b] Doubling of the signals was observed in $CDCl_3$ solution. [c] $p-CH_3C_6H_4$-signal was found at δ 20.9. [d] The signal from the RSO_2NCH_3-carbon was found at δ 31.4.

Table 2. ^{1}H NMR chemical shift values[a] in DMSO-d_6 solution

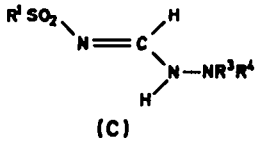
Compound		NCHN cis	NCHN trans	NH cis	NH trans	CH_3SO_2	$-NHR_2$ cis	$-NHR_2$ trans	$-NCH_3N<$	J_{CHNH} Hz cis	J_{CHNH} Hz trans	Ratio cis/trans	Coalescence Temp.[b] K
$CH_3SO_2NCHNH(CH_3)_2$	1a	7.64(s,b)	8.02(d)	9.42(s,b)	9.88(d)	2.82(s)	2.54(s)			~ 1	11.0	6/10	415
$C_6H_5SO_2NCHNH(CH_3)_2$	1b	7.87(s,b)	8.18(d)	9.7(s,b)	10.07(d)		2.53(s)			~ 1	11.0	1,5/1	408
p-$CH_3C_6H_4SO_2NCHNH(CH_3)_2$	1c	7.77(s,b)	8.11(d)	9.6(s,b)	10.04(d)		2.52(s)			~ 1	11.0	3/4	398
$CH_3SO_2NCHNH(C_2H_5)_2$	1d	7.88(s)	7.97(d)	9.1(s,b)	9.60(d)						11.0	1/3	
p-$CH_3C_6H_4SO_2NCHNH(C_2H_5)_2$	1e	8.10(s)	8.11(d)	9.28(s,b)	9.78(d)		0.93(t)	0.96(t)		~ 1	10.5	1/3	410
$C_6H_5SO_2NCHNH(CH_3)C_6H_5$	1f	8.26(s,b)	8.33(d)	10.56(s,b)	10.81(d)		3.07(s)	3.15(s)		~ 2	10.5	3/2	378
p-$CH_3C_6H_4SO_2NCHNH(CH_3)C_6H_5$	1g	8.40(d)	8.48(d)	10.70(d)	10.96(d)		3.08(s)	3.10(s)		2.5	12.0	2/1	378
$CH_3SO_2NCHNCH_3N(CH_3)_2$	1h	8.32(s)				2.98(s)	2.60(s)		2.95(s)				
$C_6H_5SO_2NCHNCH_3N(CH_3)_2$	1i	8.37(s)					2.55(s)		2.95(s)				
p-$CH_3C_6H_4SO_2NCHNCH_3N(CH_3)_2$	1j	8.28(s)					2.53(s)		2.92(s)				

[a] Centers of multiplets, multiplicity given in parenthesis. [b] Coalescence of the N=CH-N proton signals (± 10 K).

$CDCl_3$ solution. These data indicate the presence of two isomers in solution. From the ^1H data (Table 2) the ratio between the two isomers can be estimated. The magnitude of the J_{CHNH} coupling constants *ca.* 11 Hz and 1–2 Hz indicates the presence of a *trans* and a *cis* isomer.

The ratio between the *cis* and *trans* isomers was found to be solvent dependant. 1c recrystallized from ethanol gave approximately a 1/1 ratio of the two isomers which on standing for a few minutes in the NMR tube changed to ratio 3/4. Recrystallization from benzene gave almost exclusively the *cis* isomer which on standing in the tube gave the ratio 3/4 after 20 min. Similar results were found for compounds 1a and 1b.

For the formohydrazide imide form tautomer **B** there are four possible isomers C–F. To find the origin of the observed isomers some variable temperature NMR measurements were carried out, and the results were



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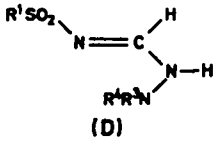

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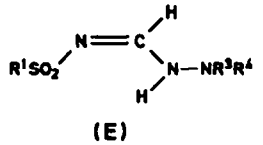

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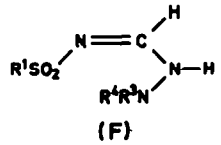

(F)

compared to the IR and ^{13}C NMR data. Table 2 shows the coalescence temperatures for the two imino CH proton signals to be from 415–378 K which correspond to a barrier to rotation similar to that found for hindered rotation in N-sulphonylamidines.[1] The IR spectrum of 1c recrystallized from ethanol and 1c recrystallized from benzene obtained in KBr, were almost identical. The only differences between the two preparations were found in the intensities of the vibrations at 3135 and 3196 cm^{-1}. Dilution experiments were carried out for compounds 1b and 1c in $CHCl_3$ to see whether the position and relative intensities of the NH stretching vibrations were concentration dependent. No changes were found on dilution in this solvent.

As is evident from Table 1 the chemical shift differences in the –N–N-part of the molecule are significantly greater than those found in the RSO_2-part for compounds exhibiting two sets of signals. This indicates that the different conformations are in the –N–N-part of the molecule, in accordance with results found for N-sulphonylformamidines.[1]

Cooling experiments for compounds 1h–1j in $CDCl_3$ solution (223 K) did not cause any changes from the room temperature spectra.

The mass spectra obtained from the prepared compounds were all in accordance with the proposed structures.

DISCUSSION

The actual tautomeric form can be easily established as a hydrazide imide from the ^{13}C NMR spectra. This tautomeric form is in contrast to the form found for formamidrazones without N″-sulphonyl group, which have been shown to exist as amide hydrazones.[2,3]

In the discrimination between the four possible isomers of the hydrazide imide form, the high temperature ^1H NMR measurements and the chemical shift differences found in the ^{13}C NMR spectra indicate the origin of the observed isomers to be hindered rotation around the CN^1 bond, so it must be one of the pairs C and D or E and F which exists in solution. Also the strong solvent dependence of the isomer ratio indicates that it is not isomerism around the CN^3 bond. The IR show the position of the NH stretching vibration around 3200 cm^{-1}, which indicates the presence of inter- or intramolecular H-bonds. As the dilution experiments show the position and relative intensities of the stretching vibration to be unaffected on dilution, it is most likely the isomers E and F which exist in solution. For the isomer F the presence of an intermolecular H-bond was to be expected. It has, however, been found for some formamidrazones[2,3] that this could not be observed in chloroform solution. For the compounds investigated here the solubility in other solvents was too low to make possible the appropriate dilution experiments.

EXPERIMENTAL

Microanalyses were carried out in the microanalysis department of Chemical Laboratory II, the H.C. Ørsted Institute. ^1H NMR spectra were obtained on a JEOL JNM 60/II instrument, ^{13}C NMR spectra were recorded on a Bruker WH 90 instrument. Mass spectra were taken on a AEI-902 instrument operating at 70 eV. IR spectra were recorded on a Perkin Elmer model 225 grating spectrograph, the values of the NH-stretching vibration and the C–N stretching/N–H bending vibration is given below. Melting points are uncorrected.

N^2,N^2-Dimethylformohydrazide methylsulphonylimide (1a). N,N-Dimethylhydrazine (0.1 mol) was added to a soln of $CH_3SO_2NCHOEt$[7] (0.1 mol) in 100 ml dry ether. After stirring for 15 min the ppt was filtered off and recrystallized from EtOH, yield 80%, m.p. 162–163°. (Found: C, 29.30; H, 6.67; N, 25.47; S, 19.21. $C_4H_{11}N_3O_2S$ requires: C, 29.08; H, 6.71; N, 25.43; S, 19.41%). MS: *m/e* (% of base peak): 165(7)M^+, 123(59), 86(22), 79(14), 60(20), 59(100), 57(9), 45(12), 44(27), 43(43), 42(25). IR(KBr, cm^{-1}): 3210m, 3150w, 1638s, 1615m.

N^2,N^2-Dimethylformohydrazide phenylsulphonylimide 1b was prepared analogous to 1a from N,N-dimethylhydrazine (0.05 mol) and $C_6H_5SO_2NCHOEt$[8] (0.05 mol), yield 58%, m.p. 116–117° from EtOH. (Found: C, 47.55; H, 5.83; N, 18.45; S, 14.00. $C_9H_{13}N_3O_2S$ requires: C, 47.56; H, 5.77; N, 18.49; S, 14.11%). MS *m/e* (% of base peak): 227(2)M^+, 157(47), 141(33), 94(19), 93(31), 78(11), 77(100), 59(28), 51(33), 50(14), 44(14), 43(14), 42(11). IR(KBr, cm^{-1}): 3190w, 3130m, 1655s, 1640m.

N^2,N^2-Dimethylformohydrazide 4-methylphenylsulphonylimide (1c). Preparation from N,N-dimethylhydrazine (0.05 mol) and *p*-$CH_3C_6H_4SO_2NCHOEt$[8] (0.05 mol) analogous to 1a, yield 75%, m.p. 158–159°. (Found: C, 49.87; H, 6.34; N, 17.27; S, 13.40; $C_{10}H_{15}N_3O_2S$ requires: C, 49.77; H, 6.27; N, 17.41; S, 13.29%). MS *m/e* (% of base peak): 241(7)M^+, 199(18), 171(34), 155(38), 108(14), 107(12), 91(100), 86(22), 71(12), 65(30), 59(50), 44(32), 43(20). IR(KBr, cm^{-1}): 3195w, 3130w, 1640s, 1625m.

N^2,N^2-Diethylformohydrazide methylsulphonylimide (1d). The mixing of N,N-diethylhydrazine and $CH_3SO_2NCHOEt$ in equimolar amounts (0.05 mol) analogous to 1a gave a compound which was contaminated with $CH_3SO_2NH_2$, yield *ca.* 50%, m.p. 69–71°. IR($CHCl_3$, cm^{-1}): 3205w, 1620s.

N^2,N^2-Diethylformohydrazide 4-methylphenylsulphonylimide (1e). N,N-Diethylhydrazine (0.044 mol) and *p*-$CH_3C_6H_4SO_2NCHOEt$ (0.044 mol) were mixed analogous to 1a, yield 47%, m.p. 134–136°. (Found: C, 53.35; H, 7.11; N, 15.15; S, 12.18. $C_{12}H_{19}N_3O_2S$ requires: C, 53.51; H, 7.11; N, 15.60; S, 11.90%). MS *m/e* (% of base peak): 269(1)M^+, 171(45), 155(37), 108(16), 107(20), 91(100), 89(11), 65(34), 56(14), 51(13). IR(KBr, cm^{-1}): 3190w, 3140w, 1650m, 1630s.

N²-Methyl-N²-phenylformohydrazide phenylsulphonylimide (1f). Preparation from N-methyl-N-phenylhydrazine (0.05 mol) and $PhSO_2NCHOEt$ (0.05 mol) analogous to 1a gave a yield of 20%, m.p. 167–169° from EtOH. From the filtrate of the reaction-mixture 3.5 g of benzenesulfonamide could be isolated (identified by IR spectrum). (Found: C, 58.05; H, 5.25; N, 14.66; S, 11.06; $C_{14}H_{15}N_3O_2S$ requires: C, 58.11; H, 5.23; N, 14.52; S, 11.08%). MS *m/e* (% of base peak): 289(32)M⁺, 148(36), 141(11), 122(16), 121(59), 107(16), 106(45), 105(100), 104(25), 92(16), 78(16), 77(98), 51(32). IR(KBr, cm^{-1}): 3280s, 3240shw, 1605s, 1598s.

N²-Methyl-N²-phenylformohydrazide 4-methylphenylsulphonylimide (1g) was prepared from N-methyl-N-phenylhydrazine (0.05 mol) and p-$CH_3C_6H_4SO_2NCHOEt$ (0.05 mol) as for 1a, yield 33%, m.p. 178–179°. (Found: C, 59.55; H, 5.53; N, 13.89; S, 10.84. $C_{15}H_{17}N_3O_2S$ requires: C, 59.38; H, 5.65; N, 13.85; S, 10.57%). MS *me* (% of base peak): 303(38)M⁺, 155(10), 148(52), 122(20), 121(75), 107(17), 106(55), 105(100), 104(30), 92(15), 91(55), 77(55), 65(23), 51(15). IR(KBr, cm^{-1}): 3195m, 3140w, 1618s, 1600m.

N¹-Methyl-N²,N²-dimethylformohydrazide methylsulphonylimide (1h). Trimethylhydrazine[9] (0.05 mol) was slowly added to a soln of $CH_3SO_2NCHOEt$ (0.05 mol) in 70 ml ether. After stirring for 1.5 hr at room temp. the mixture was cooled with ice, and the ppt was filtered off and recrystallized from EtOH, yield 62%, m.p. 89–91°. (Found: C, 33.35; H, 7.21; N, 23.19; S, 17.95. $C_5H_{13}N_3O_2S$ requires: C, 33.51; H, 7.31; N, 23.44; S, 17.89%). MS *m/e* (% of base peak): 179(1)M⁺, 137(17), 79(14), 73(57), 59(23), 57(19), 44(100), 43(37), 42(56). IR(KBr, cm^{-1}): 1605s.

N¹-Methyl-N²,N²-dimethylformohydrazide phenylsulphonylimide (1i). Trimethylhydrazine (0.047 mol) and $PhSO_2NCHOEt$ (0.047 mol) were mixed analogous to the procedure for 1h, yield 35%, m.p. 86–88°. (Found: C, 49.77; H, 6.40; N, 17.15; S, 13.44. $C_{10}H_{15}N_3O_2S$ requires: C, 49.77; H, 6.27; N, 17.41; S, 13.29%). MS *m/e* (% of base peak): 241(1)M⁺, 199(20), 141(11), 133(65), 77(53), 73(58), 59(15), 57(15), 51(20), 44(100). IR(KBr, cm^{-1}): 1600s, broad.

N¹-Methyl-N²,N²-dimethylformohydrazide 4-methylphenylsulphonylimide (1j). Preparation from trimethylhydrazine (0.05 mol) and p-$CH_3C_6H_4SO_2NCHOEt$ (0.05 mol) analogous to 1h gave a yield of 57%, m.p. 146–148° from EtOH. (Found: C, 51.80; H, 6.83; N, 16.35; S, 12.68. $C_{11}H_{17}N_3O_2S$ requires: C, 51.74; H, 6.71; N, 16.46; S, 12.56%). MS *m/e* (% of base peak): 255(1)M⁺, 213(18), 155(14), 148(16), 147(66), 91(64), 74(14), 73(80), 65(20), 59(16), 57(20), 44(100), 43(22), 42(28). IR(KBr, cm^{-1}): 1600s, broad.

N¹,N²-Dimethyl-N²-phenylformohydrazide phenylsulphonylimide (1k). N^1,N^2-Dimethyl-N^1-phenylhydrazine (0.046 mol) was slowly added dropwise to a soln of $PhSO_2NCHOEt$ (0.046 mol) in 70 ml dry ether. After stirring for 4 days the ppt was filtered off, yield 85%, m.p. 118–120° from EtOH. (Found: C, 59.30; H, 5.81; N, 13.82; S, 10.47. $C_{15}H_{17}N_3O_2S$ requires: C, 59.38; H, 5.65; N, 13.85; S, 10.57%). MS *m/e* (% of base peak): 303(4)M⁺, 199(21), 135(32), 105(14), 104(18), 78(14), 77(100), 59(21), 51(32). IR(KBr, cm^{-1}): 1595s, broad. ^1H NMR (DMSO-d_6): δ 8.63 (s) and 8.60 (s) (1 H, intensity 1/2), 3.13 (s) and 3.03 (s) (3 H, intensity 1/2), 3.37 (s) and 3.22 (s) (3 H, intensity 1/2).

N^1,N^2-Dimethyl-N^3-phenyl-N^1-(4-methylphenylsulphonyl) formamide hydrazone (2). N,N' - Dimethyl - N - phenylformamidrazone[10] (0.033 mol), p-toluene-sulphonylchloride (0.033 mol) and triethylamine (0.066 mol) were mixed in 70 ml benzene. After stirring overnight at room temp. the ppt was filtered off and the components were isolated by PLC on silicagel, yield of 2 5%, m.p. 84°. MS *m/e* (% of base peak): 317(53)M⁺, 163(13), 162(55), 122(11), 121(100), 120(13), 107(11), 106(27), 105(13), 92(18), 91(29), 77(45), 65(13). IR($CHCl_3$, cm^{-1}): 1602s. ^1H NMR (DMSO-d_6): δ 7.78 (1 H, s), 7.7–7.0 (9 H, m), 3.25 (3 H, s), 2.93 (3 H, s), 2.37 (3 H, s).

N^1,N^2-Dimethyl-N^1-phenylhydrazine was prepared analogous to trimethylhydrazine,[11] yield 75%, m.p. 49–51°/0.45 mmHg.[11]

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