*Chemistry of Heterocyclic Compounds, Vol. 31, No. 9, 1995*

# MESOIONIC COMPOUNDS — STRUCTURE AND NMR PARAMETERS

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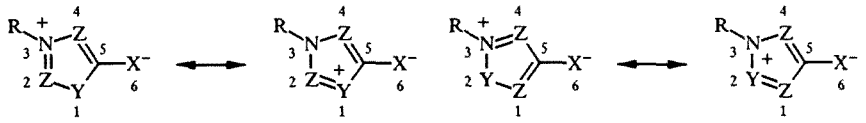
*It has been shown that $^{1}H$, $^{13}C$, $^{14}N$, $^{15}N$, $^{17}O$, and $^{77}Se$ NMR are very successful techniques for the identification and investigation of potential valence tautomerism in all types of mesoionic compounds. Especially the combined use of $^{14}N$ and $^{15}N$ NMR studies has been shown to be very effective in solving structural problems. From $^{15}N$ NMR it is possible to obtain accurate chemical shifts and spin-spin couplings, whereas the $^{14}N$ NMR spectra provide us with nuclear relaxation and some chemical shift data. In particular $^{14}N$ NMR is very useful for the identification of charged nitrogen atoms in molecules containing non equivalent nitrogen positions. This information is available from the relative $^{14}N$ signal widths, which depend upon the rates of $^{14}N$ relaxation, positively charged nitrogen atoms usually have relatively slow $^{14}N$ relaxation rates thus giving rather sharp NMR signals. Some solid state, CP MAS, $^{13}C$ and $^{15}N$ NMR results are available for comparison with the solution NMR data.*

This paper contains the results of a wide study of NMR spectral parameters in relation to structural problems of "so called" mesoionic heteroaromatic compounds published from 1974 to 1995 [1-44]. The nitrogen NMR ($^{14}N$ and $^{15}N$) techniques are our main interest. Some $^{1}H$, $^{13}C$, $^{17}O$, and $^{77}Se$ NMR data are also included. Mesoionic compounds are heteroaromatic structures having a five membered ring containing two, three or four heteroatoms. This group of compounds is divided into two classes: compounds of type A and type B. The basis of those classes is as follow: two heteroatoms with formal positive charge, providing three p-electrons for the delocalized $\pi$-electron system. The formal positive charge may be either on atoms 1 and 3, or on atoms 2 and 3 in the five membered ring, for type A or type B compounds, respectively. The substituent possessing a formal negative charge is at the 5 position (Scheme 1).

Scheme 1



A B

Mesoionic compounds of types A and B
X = O, S, Se, NR, $CR_2$ and others; Y = O, S, NR; Z = N, CR

The structures of this type can be regard as an azolium cation with an anionic substituent. Thus the total electric charge of the molecule is equal to zero. However, it is not evident whether $\pi$-electron system is able to accomplish the supposition. It is possible to construct an analogical isomeric open-chain structure, without a formal charge separation. Thus, the real structure

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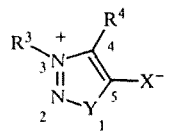
0009-3122/95/3109-1027$12.50 

TABLE 1. NMR Spectral Parameters of Some Type A Mesoionic Compounds with Three Heteroatoms in 1, 2, and 3 positions



| $X^-$, $R^3$, $R^4$ | Y[a] | $N^{2b}$ | $N^{3b}$ | $C^{4c}$ | $C^{5c}$ | 5-exo[a, b, c] | Solvent[d] | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| | | | $X^-$ = $O^-$, Y = O, $R^4$ = H | | | | | |
| $R^3$ = Me | 387(330)[e] | | | | | 209(250)[f] (O) | Methanol/water | [10] |
| | 389[g] | | | | | 232(150)[e] (O) | | [6] |
| | | | | | | 234[g] (O) | | [9] |
| | | | -108(24)[h] | | | | Acetone | [4] |
| | | -36,2 | -112,5 | | | | Acetone | [8] |
| | | -34,7(500)[h] | -107,8(22)[h] | | | | | |
| | | | | 97,3 | 170,4 | | Water | [2] |
| | | | | 96,8 | 169,2 | | Chloroform | [1] |
| $R^3$ = Et | | -36,9 | -99,1 | | | | Acetone | [4, 8] |
| | | | -97(29)[h] | | | | | |
| | | | -96(106)[h,i] | | | | | |
| $R^3$ = *i*-Pr | | -35,3 | -85,7 | | | | Acetone | [4, 8] |
| | | | -84(35)[h] | | | | | |
| $R^3$ = Ph | 388(370) | | | | | 244(250) (O) | Benzene | [18] |
| | 388(260)[j] | | | | | 242[j] (O) | 85[o] | |
| | | | -98(28)[h] | | | | Acetone | [4, 8] |
| | | | -94(43)[h, k] | | | | | |

TABLE 1 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| | | | | $X^-$ = $O^-$, Y = O | | | | |
| $R^3$ = Ph<br>$R^4$ = Br | | | -100(92) | | | | Acetone | [4, 8] |
| $R^3$ = Ph<br>$R^4$ = $NO_2$ | | | -101(80) | | | | Acetone | [4, 8] |
| $R^3$, $R^4$ [l] | | | | 93...109[l] | 162...176[l] | | | [13, 21, 22] |
| | | | | $X^-$ = OH/Cl⁻, Y = O, $R^4$ = H | | | | |
| $R^3$ = Me | | | -94(270)[h] | | | | Methanol | [4, 8] |
| | | | | | | 188(1492) (O) | TFA | [10] |
| | | -32,2 | | | | | Acetone | [7] |
| | | -29,0 | | 98,7 | 172,2 | | Methanol/water | [10, 17] |
| | | | | 104,5 | 170,1 | | Water | [2] |
| | | | | $X^-$ = $NH_2$/Cl⁻, Y = O, $R^4$ = H | | | | |
| $R^3$ = Me | | -16,0 | -105,8<br>-106(150)[h] | | | -309,5 (N) | Methanol | [4, 8] |
| | | -15,0[i] | -104,0[m] | | | -307,3[m] (N)<br>$^1J_{NH}$ = 96,8 Hz | Methanol | [17] |
| | | -15,0 | -104,9 | | | -309,2 (N) | Methanol/water | [17] |
| | | | | 104,5 | 170,5 | | Methanol/water | [10] |
| $R^3$ = Ph | | | -96(260)[h] | | | | Methanol | [4, 8] |
| | 348(310) | | | | | | Water-$^{16}$O | [18] |
| | | | | $X^-$ = $NH_2$/Cl⁻, Y = O, $R^4$ = *i*-Pr | | | | |
| $R^3$ = Ph | 350(350) | | | | | | Water-$^{16}$O | [18] |

TABLE 1 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| | | | | $X^-$ = $N^-COCH_3$, Y = O, $R^4$ = H | | | | |
| $R^3$ = Me | | -27(450) [h] | -109(450) [h] | | | -205(500) [h] (N) | Acetone | [4, 8] |
| | | -22,7 | -105,5 | | | -203,6 (N) | Methanol | [7, 17] |
| | | -33,6 | -111,2 | | | -197,5 (N) | Acetone | [7, 17] |
| $R^3$ = Et | | | -97(65) [h] | | | | Acetone | [4, 8] |
| | | | -97(340) [h, n] | | | | | |
| | | -33,0 | -97,1 | | | -197,2 (N) | Acetone | [7, 17] |
| $R^3$ = *i*-Pr | | | -86(75) [h] | | | | Acetone | [4, 8] |
| | | -31,7 | -85,0 | | | -196,2 (N) | Acetone | [7, 17] |
| | | | | $X^-$ = $NHCOCH_3/Cl^-$, Y = O, $R^4$ = H | | | | |
| $R^3$ = Me | | -6,5 | -100,4 | | | -252,2 (N) | Methanol | [4, 8] |
| | | -5,5 [o] | -98,9 [o] | | | -250,0 [o] (N) | | |
| | | | -104(250) [h] | | | | | |
| $R^3$ = Et | | -9,6 | -88,1 | | | -252,2 (N) | Methanol | [4, 8] |
| | | | -92(300) [h] | | | | | |
| $R^3$ = *i*-Pr | | -9,6 | -79,7 | | | -251,5 (N) | Methanol | [4, 8] |
| | | | -84(380) [h] | | | | | |
| | | | | $X^-$ = $C^-(CN)_2$, Y = O, $R^4$ = H | | | | |
| $R^3$ = Ph | 339(360) | | | | | | Acetonitrile 80° | [18] |
| | | | | Y = S, $R^3$ = Me, $R^4$ = H | | | | |
| $X^-$ = $N^-Ph$ | — | -118,0 ? | -116,1 | | | -147,3 (N) | DMSO-$d_6$ | [27] |
| $X^-$ = $NHPh/BF_4^-$ | — | -69,3 ? | -107,2 | | | -268,8 (N) | DMSO-$d_6$ | [27] |
| $X^-$ = — C(H)=N— $O^-$ | — | -35,8 | -121,1 | | | 96,4 (N)<br>$^2J$NO— CH = 11,2 Hz | DMSO-$d_6$ | [27] |
| $X^-$ = — C(H)=N— $N^-Ph$ | — | -37,6 | -131,2 | | | 16,5 (N)<br>$^2J$N— CH = 10,8 Hz<br>-52,8 (NPh) | Chloroform | [27] |

TABLE 1 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| | | | | Y = S, $R^3$ = Me, $R^4$ = H | | | | |
| $X^-$ – C(H)=N– $O^-$ | – | -36,5 | -124,3 | | | 97,5 (N)<br>$^2J_{NO-CH}$ = 10,8 Hz | DMSO-d6 | [27] |
| $X^-$ – C(H)=N– $N^+$Ph | – | -34,5 | -133,5 | | | 16,9 (N)<br>$^2J_{N-CH}$ = 11,2 Hz<br>-56,8 (NPh) | Chloroform | [27] |
| | | | | $X^-$ = $O^-$, Y = $NR^1$, $R^3$ = Me, $R^4$ = H | | | | |
| $R^1$ = Ph | | | | 107,9 | 158,1 | | Chloroform | [16] |
| $R^1$ = o-$MeC_6H_4$ | | | | 107,8 | 158,2 | | Chloroform | [16] |
| | | | | $X^-$ = $N^-C(=O)CH_3$, Y = $NR^1$, $R^3$ = Me, $R^4$ = H | | | | |
| $R^1$ = Ph | | | | 117,8 | 151,4 | | Chloroform | [16] |
| $R^1$ = o-$MeC_6H_4$ | | | | 117,6 | 150,9 | | Chloroform | [16] |
| $R^1$ = o-$ClC_6H_4$ | | | | 117,9 | 151,5 | | Chloroform | [16] |

[a] $^{17}O$ NMR chemical shift (ppm) with respect to $H_2O$ signal (0 ppm) and signal half-width (Hz) in parenthesis.

[b] $^{15}N$ NMR chemical shift (ppm) with respect to $CH_3NO_2$ signal (0 ppm).

[c] $^{13}C$ NMR chemical shift (ppm) with respect to $(CH_3)_4Si$ signal (0 ppm).

[d] Abbreviations: TFA-trifluoroacetic acid; DMSO-dimethylsulfoxide.

[e] Ref. 6.

[f] Ref. 10.

[g] Ref. 9.

[h] $^{14}N$ NMR chemical shift (ppm) with respect to $CH_3NO_2$ signal (0 ppm) and signal half-width (Hz) in parenthesis; more $^{14}N$ NMR data of large number of compounds with various $R^3$ groups are reported in Ref. 4, 8.

[i] Neat compound.

[j] $^{17}O$ labeled compound.

[k] $CHCl_3$ solution.

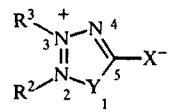
[l] The compiled data for a large group of compounds with various $R^3$ and $R^4$ groups. Ref. 13, 21, 22.

[m] The $^{15}N$-$^{13}C$ coupling constants; $^2J$N2–C5 = 2.2 Hz, $^1J$N3–C4 = 12.4 Hz, $^1J$Nexo–C5 = 23.5 Hz; Ref. 10.

[n] $CH_3OH$ solution.

[o] Ref. 17.

TABLE 2. NMR Spectral Parameters of Some Type A Mesoionic Compounds with Three Heteroatoms in 1, 3, and 4 positions



| $X^-$ | $R^1$ | $R^2$ | $R^3$ | $N1^a$ | $N3^a$ | $N4^a$ | $C2^b$ | $C5^b$ | $5\text{-exo}^{a,b,c}$ | Solvent[d] | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| | | | | | **Y = $NR^1$** | | | | | | |
| $N^-Ph$ | Ph | H | Ph | -210,5 | -170,9 | -155,8 | 150,4 | 153,9 | -235,7 (N) | DMSO-$d_6$ | [42] |
| | | | | -209,4 | -165,7 | -139,6 | | | -298,7 (N) | TFA-$d_1$ | [42] |
| $N^-(Me)Ph/I^-$ | Ph | H | Ph | -203,6 | -164,2 | -123,3 | 141,1 | 153,4 | -315,9 (N) | DMSO-$d_6$ | [42] |
| $S^-$ | Ph | Ph | Ph | -182,5 | -164,1[e] | -102,5 | 148,1 | 169,8 | | DMSO-$d_6$ | [42] |
| $S^-$ | Ph | Ph | Ph | -181,6[f] | | | 148,2 | 169,9 | | DMSO-$d_6$ | [32] |
| $S^-$ | Ph | Ph | Ph | -185,0 | -164,9 | -98,0 | 149,8 | 170,6 | | Solid state | [32] |
| $S^-$ | Ph | Ph | Me | -186,0 (1700) | -176,6[e] | -102,5[e] | 147,6 | 169,6 | | DMSO-$d_6$ | [42] |
| $S^-$ | Me | Ph | Me | -205,0[e] (1800) | -178,7[e] | -100,8[e] | 147,3 | 169,0 | | DMSO-$d_6$ | [42] |
| $S^-$ | Ph | Me | Me | -186,3 (1800) | -179,1 | -104,3[e] | 147,2 | 168,4 | | DMSO-$d_6$ | [42] |
| | | | | -191,2 | -170,5 | -96,6 | | | | TFA-$d_1$ | [42] |
| $S^-$ | Ph | $p$-$MeOC_6H_4$ | Ph | -182,0[g] | -163,9[g] | -102,0[g] | 148,3 | 169,7 | | DMSO-$d_6$ | [32] |
| $S^-$ | Ph | $p$-$MeOC_6H_4$ | Ph | -185,5 | -165,1 | -102,2 | 148,9 | 169,2 | | Solid state | [32] |

TABLE 2 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $S^-$ | Ph | $p$-$NO_2C_6H_4$ | Ph | -181,5[h] | -162,2[h] | -100,4[h] | 146,4 | 170,4 | | DMSO-d6 | [32] |
| $S^-$ | Ph | $p$-$NO_2C_6H_4$ | Ph | -185,2 | -162,1 | -96,6 | | | | Solid state | [32] |
| $S^-$ | Me | Me | Me | -205,3[e] | -181,3 | -103,0[e] | 146,9 | 167,8 | | DMSO-d6 | [42] |
| SMe/$I^-$ | Ph | Ph | Ph | -191,9 | -157,3 | -98,2 | 152,1 | 156,1 | | DMSO-d6 | [42] |
| SMe/$I^-$ | Me | Ph | Ph | -206,1[e] | -158,1[e] | -95,6 | 152,2 | 155,4 | | DMSO-d6 | [42] |
| SMe/$I^-$ | Ph | Ph | Me | -193,8 (2000) | -168,3[e] | -98,4[e] | 151,8 | 155,2 | | DMSO-d6 | [42] |
| SMe/$I^-$ | Me | Ph | Me | -208,3[e] | -169,5 | -95,4[e] | 151,8 | 154,6 | | DMSO-d6 | [42] |
| SMe/$I^-$ | Ph | Me | Me | -194,5 (2100) | -169,9 | -99,3[e] | 153,2 | 153,9 | | DMSO-d6 | [42] |
| SMe/$I^-$ | Me | Me | Me | -208,9 (1000) | -171,1 (1500) | -96,7[e] | 152,9 | 153,1 | | DMSO-d6 | [42] |
| $C^-(CN)_2$ | Ph | Ph | Ph | -204,9 | -163,4 | -122,1 | 148,8 | 155,9[i] | -116,0 (CN) 119,4 (CN) 22,1[i] ($C^-$) | DMSO-d6 | [42] |
| $C^-(CN)(COOEt)$ | Ph | Ph | Ph | -198,1 | -161,8[e] | -121,7 | 148,7 | 155,7[i] | -108,3 (CN) 121,9 (CN) 44,2[j] ($C^-$) 166,3 (CO) | DMSO-d6 | [42] |
| $Se^-$ | Ph | Ph | Me | -180,9 | -171,3[e] | -92,9[e] | 148,9 | 161,0 | 24,9[k] (Se) | DMSO-d6 | [42] |
| $Se^-$ | Ph | Me | Me | -181,3[e] | -173,7[e] | -94,5[e] | 148,7 | 159,3 | 19,66[l] (Se) | DMSO-d6 | [43] |
| SMe/$I^-$ | Ph | Ph | Me | -188,9 | -165,4e | -91,6[e] | 152,2 | 149,2 | 198,6[m] (Se) | DMSO-d6 | [43] |
| SMe/$I^-$ | Ph | Me | Me | -189,4[e] | -167,0[e] | -92,0[e] | 153,3 | 147,4 | 193,9[n] (Se) | DMSO-d6 | [43] |
| $SeI_2^-$ | Ph | Me | Me | -184,3[e] | -166,2[e] | -77,8[e] | 153,2 | 145,8 | 334,1 (Se) | DMSO-d6 | [43] |
| | | | | | Y = S | | | | | | |
| $N^-Ph$ | — | Ph | Ph | | | | | 152,1 | -183,2[o] (N) | Chloroform-d1 | [32] |
| $N^-Ph$ | — | $p$-$MeOC_6H_4$ | Ph | | -145,5[p] | -115,5[p] | 162,0 | 152,3 | -184,4 (N) | Chloroform-d1 | [32] |

TABLE 2 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $N^-Ph$ | — | $p$-$NO_2C_6H_4$ | Ph | | -137,8[r] | -109,4 | 159,9 | 152,1 | -181,5[r] (N) | Chloroform-$d_1$ | [32] |
| $NHPh/Cl^-$ | — | Ph | Ph | | -145,4[s] | | | | -270,1[s] (N) | DMSO-$d_6$ | [32] |
| $NHPh/Cl^-$ | — | Ph | Ph | | -148,6 | -101,4 | | | -269,3 (N) | Solid state | [32] |
| $NHPh/Cl^-$ | — | $p$-$MeOC_6H_4$ | Ph | | -149,6[t] | -100,6 | | | -270,1[t] (N) | DMSO-$d_6$ | [32] |
| $NHPh/Cl^-$ | — | $p$-$MeOC_6H_4$ | Ph | | -155,4 | -102,9 | | | -268,7 (N) | Solid state | [32] |
| $NHPh/Cl^-$ | — | $p$-$NO_2C_6H_4$ | Ph | | -142,7[u] | -101,3[u] | | | -268,1[u] (N) | DMSO-$d_6$ | [32] |
| $NHPh/Cl^-$ | — | $p$-$NO_2C_6H_4$ | Ph | | -148,3 | -98,7 | | | -256,0 (N) | Solid state | [32] |

[a] $^{15}N$ NMR chemical shift (ppm) with respect to $CH_3NO_2$ signal (0 ppm) and $^{14}N$ NMR signal half-width (Hz).

[b] $^{13}C$ NMR chemical shift (ppm) with respect to $(CH_3)_4Si$ signal (0 ppm).

[c] $^{77}Se$ NMR chemical shift (ppm) with respect to $(CH_3)_2Se$ signal (0 ppm).

[d] Abbreviations: TFA = trifluoroacetic acid; DMSO — dimethylsulfoxide.

[e] $^nJ$15N-1H coupling constants (Hz) of side groups, ~1-3 Hz.

[f] $^{15}N$-$^{13}C$ coupling constants; $^1J$N1-C5 = 4.0 Hz, $^1J$N1-C2 = 19.2 Hz, $^1J$N1-C(i) = 16.1 Hz.

[g] $^{15}N$-$^{13}C$ coupling constants; $^1J$N1-C5 = 4.0 Hz, $^1J$N1-C2 = 18.1 Hz, $^1J$N1-C(i) = 16.1 Hz, $^1J$N3-C2 = 19.1 Hz, $^1J$N3-C(i) = 19.1 Hz, $^1J$N4-C5 = 3.0 Hz.

[h] $^{15}N$-$^{13}C$ coupling constants; $^1J$N1-C5 = 4.0 Hz, $^1J$N1-C2 = 20.1 Hz, $^1J$N3-C(i) = 16.1 Hz, $^1J$N3-C2 = 20.1 Hz, $^1J$N3-C(i) = 18.1 Hz, $^1J$N4-C5 = 3.0 Hz.

[i] $^{13}C$-$^{13}C$ coupling constants; $^1J$C5-C$^-$ = 96.8 Hz, $^1J$C$^-$-CN = 98.0 Hz.

[j] $^{13}C$-$^{13}C$ coupling constants; $^1J$C5-C$^-$ = 91.4 Hz, $^1J$C$^-$-CN = 93.5 Hz.

[k] $^{77}Se$-$^{13}C$ and $^{77}Se$-$^{15}N$ coupling constants; $^1J$Se-C5 = 228.9 Hz, $^3J$Se-N3 = 5.1 Hz.

[l] $^{77}Se$-$^{13}C$ and $^{77}Se$-$^{15}N$ coupling constants; $^1J$Se-C5 = 227.1 Hz, $^3J$Se-N3 = 4.9 Hz.

[m] $^{77}Se$-$^{13}C$ and $^{77}Se$-$^{15}N$ coupling constants; $^1J$Se-C5 = 164.3 Hz, $^3J$Se-N3 = 5.5 Hz, $^1J$Se-CH3 = 56.0 Hz.

[n] $^{77}Se$-$^{13}C$ and $^{77}Se$-$^{15}N$ coupling constants; $^1J$Se-C5 = 163.1 Hz, $^3J$Se-N3 = 5.5 Hz, $^1J$Se-CH3 = 55.9 Hz.

[o] $^{15}N$-$^{13}C$ coupling constant; $^1J$Nexo-C(i) = 16.6 Hz.

[p] $^{15}N$-$^{13}C$ coupling constants; $^1J$N4-C5 = 36.6 Hz, $^1J$N3-C2 = 15.3 Hz, $^1J$N3-C(i) = 17.1 Hz.

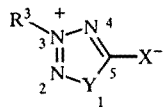
[r] $^{15}N$-$^{13}C$ coupling constants; $^1J$Nexo-C5 = 30.0 Hz, $^1J$Nexo-C(i) = 20.1 Hz, $^1J$N3-C2 = 14.1 Hz, $^1J$N3-C(i) = 16.1 Hz.

[s] $^{15}N$-$^{13}C$ coupling constants; $^1J$Nexo-C5 = 23.1 Hz, $^1J$Nexo-C(i) = 15.1 Hz, $^1J$N3-C2 = 18.1 Hz, $^1J$N3-C(i) = 16.1 Hz.

[t] $^{15}N$-$^{13}C$ coupling constants; $^1J$Nexo-C5 = 23.1 Hz, $^1J$Nexo-C(i) = 14.1 Hz, $^1J$N3-C2 = 14.1 Hz, $^1J$N3-C(i) = 16.1 Hz.

[u] $^{15}N$-$^{13}C$ coupling constants; $^1J$Nexo-C5 = 23.1 Hz, $^1J$Nexo-C(i) = 14.1 Hz, $^1J$N3-C2 = 16.1 Hz, $^1J$N3-C(i) = 16.1 Hz.

TABLE 3. NMR Spectral Parameters of Some Type A Mesoionic Compounds with Four Heteroatoms in the Ring



| $X^-$ | $Y^{a,b}$ | $N2^b$ | $N3^b$ | $N4^b$ | $C5^c$ | 5-exo$^{a,b,c}$ | Solvent$^d$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| | | | | **Y = O, $R^3$ = Ph** | | | | |
| $O^-$ | 360(400) | -8,8 (905) | -71,6 (50) | -154,8(865) | 166,2 | 220 (O) (100) | Acetone-$d_6$ | [26] |
| $S^-$ | 398(400) | 12,9 (1200) | -64,5 (70) | -107,5(1200) | 193,4 | | Acetone-$d_6$ | [19, 26] |
| $S^-$ | | 11,8 | -63,5 | -110,2 | 192,2 | | Solid state (CP MAS) | [39] |
| $SEt/BF_4^-$ | | 22,3 | -62,9 (500) | -101,4 | 188,7[e] | | Acetone-$d_6$ | [19, 26] |
| $NH^-$ | | -17[f] (900) | -71[f] (40) | -145[f](640) | 167,2 br | -242[f] (N) (540) | DMSO-$d_6$ | [44] |
| $NH_2/Cl^-$ | | -4,4 | -69,7 (640) | -139,3 | 172,0 | -265,5 (N) br | DMSO-$d_6$ | [44] |
| $N^-Ph$ | | -18,2 | -72,4 (450) | -143,3 | 162,4 br | -210,0 (N) | DMSO-$d_6$ | [44] |
| $N^-COPh$ | | -8,6 | -71,0 (430) | -133,0 | 171,2 | -210,8 (N)<br>172,5 (C=O) | DMSO-$d_6$ | [44] |
| | | | | **Y = S, $R^3$ = Ph** | | | | |
| $O^-$ | | -39,6 (600) | -74,2 (60) | -95,2 (650) | 180,5 | 307 (O) (140) | Acetone-$d_6$ | [19,26] |
| $OEt/BF_4^-$ | | -39,4 (1500) | -74,7 (300) | -95,1 | 190,2[e] | | Acetone-$d_6$ | [19,26] |
| $S^-$ | | -24,7 (760) | -66,9 (85) | -53,9 (1260) | 201,5 | | Acetone-$d_6$ | [26] |
| $SEt/BF_4^-$ | | -9,4 (1630) | -68,6 (340) | -54,4 | 192,2[e] | | Acetone-$d_6$ | [26] |
| $N^-Ph$[g] | | -66,9 | -74,1 (340) | -90,9 | 168,0 | -144,4[h] br (NPh) | DMSO-$d_6$ | [31] |

TABLE 3 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| | | | | Y = S, $R^3$ = Ph | | | | |
| NHPh/$Cl^-$[g] | | −32,0[h] br | −78,9 (1500) | −95,5 | 173,9 | −261,0[h] (NHPh)<br>$^1J_{NH}$ = 82 Hz | DMSO-$d_6$ | [31] |
| NPhMe/$I^-$ | | −35,1 | −74,8 (1000) | −87,2 | 181,1[e] | −272,8 (NMePh) | DMSO-$d_6$ | [31] |
| $N^-$Ts | | −35,9 | −76,9 (900) | −90,3 | 179,3 | −118,6 (NTs) | DMSO-$d_6$ | [31] |
| $C^-(CN)_2$ | | −39,3 | −70,4 (720) | −78,6 | 182,4;<br>$^1J_{C5,C^-}$ = 92,7[i] | −108,1, −113,4[j] (CN)<br>117,0, 114,5[j] (CN)<br>40,7 ($C^-$) | DMSO-$d_6$ | [31] |
| | | −50,6 | −70,9[l] (700) | −81,6 | 182,0 | −116,6, −110,5[j] (CN)<br>116,7, 114,1[j] (CN)<br>40,8 ($C^-$) | Chloroform-$d_1$ | [37] |
| | | −45,5 | −73,1 | −76,9 | 182,8 | −114,1, −112,2[j] (CN)<br>116,8[k] (CN)<br>43,9 ($C^-$) | Solid state (CP MAS) | [39] |
| C(CN)(COOEt) | | −34,8 | −75,0 (766) | −83,4 | 178,4;<br>$^1J_{C5,C^-}$ = 89,2[i] | −113,9 (CN)<br>115,5 (CN)<br>168,9 (CO)<br>63,2 ($C^-$) | DMSO-$d_6$ | [31] |
| | | −39,9 | −76,9[l] (287) | −85,9 | 177,9;<br>$^1J_{C5,C^-}$ = 89,1[n] | −119,6 (CN); 115,2 (CN)<br>169,5 (CO); 65,4 ($C^-$) | Chloroform-$d_1$ | [37] |
| | | −41,5 | −74,7 | −83,6 | 178,9 | −116,1 (CN); 117,3 (CN)<br>169,9 (CO); 64,8 ($C^-$) | Solid state (CP MAS) | [39] |
| $C^-(COOEt)_2$ | | −40,2 | −77,5 (390) | −97,6 | 176,9; $^1J_{C5,C^-}$ = 82,0[i] | 170,0, 162,3[j] (CO),84,6 ($C^-$) | DMSO-$d_6$ | [31] |
| | | −40,3 | −78,2[l] (420) | −83,3 | 177,1 | 170,3, 163,1[j] (CO), 85,3 ($C^-$) | Chloroform-$d_1$ | [37] |
| | | −40,7 | −77,6 | −84,5 | 176,5 | 171,0, 161,2[j] (CO), — ($C^-$)[m] | Solid state (CP MAS) | [39] |
| $C^-(CO_2(Me)_2CO_2)$ | | −38,3 | −78,2[l] (368) | −81,1 | 176,1; $^1J_{C5,C^-}$ = 83,1[l] | 167,5, 158,1[j] (CO), 80,1 ($C^-$) | Chloroform-$d_1$ | [37] |
| $C^-$(COMe)(COEt) | | −32,1 | −80,9[l] (377) | −78,2 | 174,6; $^1J_{C5,C^-}$ = 78,6[i]<br>$^1J_{C5,C^-}$ = 78,7[n] | 191,2, 164,1 (CO), 98,1 ($C^-$) | Chloroform-$d_1$ | [37] |

TABLE 3 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| $C^-(COMe)_2$ | | -31,3 | -82,8[l] (217) | -83,2[l] | 175,4; $^1J_{C5,C^-}$ = 75,1[i] | 192,6, 192,3[j] (CO), 108,3 ($C^-$) | Chloroform-d1 | [37] |
| $C^-(COMe)(COPh)$ | | -37,1 | -82,3[l] (430) | -81,5 | 174,4; $^1J_{C5,C^-}$ = 75,6[i] | 192,0, 191,1[j] (CO), 106,8 ($C^-$) | Chloroform-d1 | [37] |
| $C^-(COPh)_2$ | | -35,9 | -80,6[l] (452) | -80,0 | 175,1; $^1J_{C5,C^-}$ = 75,6[i] | 192,6, 186,5[j] (CO), 106,2 ($C^-$) | Chloroform-d1 | [37] |
| $C^-(COMe)(CONHPh)$ | | -31,2 | -82,1[l] (334) | -87,4[l] | 176,7 $^1J_{C5,C^-}$ = 82,6[i] | -257,6 (NH) 192,4, 167,0 (CO) 96,7 ($C^-$) $^1J_{NH}$ = 88,6 Hz | Chloroform-d1 | [37] |
| | | | | Y = NPh, $R^3$ = Ph | | | | |
| $O^-$ | -163,1 (1760) | -52,4 (2940) | -108,9 (360) | -121,4 | 158,8 159,3[o] | | DMSO-d6 | [33] |
| $OEt/BF_4^-$ | -158,4 | -36,8 | -103,4 (550) | -112,7 | 160,6[e] | | DMSO-d6 | [33] |
| $S^-$ | -135,8 | -34,9 | -99,2 (1800) | -83,9 | 173,7 | | DMSO-d6 | [33] |
| $SEt/BF_4^-$ | -139,8 | -26,8 | -93,2 (3600) | -83,8 | 162,7[e] | | DMSO-d6 | [33] |
| $SC^-(CN)_2$ | | | | | 165,7 | 124,0 (CN) 5,3 ($C^-$) | DMSO-d6 | [14] |
| $C^-(CN)_2$ | -161,4 | -34,7 | -97,9 (1100) | -104,6 | 160,9 $^1J_{C5,C^-}$ = 98,9[i] | -114,8 (CN) 117,1 (CN) 24,8 ($C^-$) | DMSO-d6 | [33] |
| $C^-(CN)_2$ | | | | | 160,9 | 117,2 (CN) 25,0 ($C^-$) | DMSO-d6 | [15] |
| $C^-(CN)(COOEt)$ | -158,1 (1200)[p] | -37,0 (1800)[p] | -97,5 (1730) (650)[p] | -97,5 | 159,9 $^1J_{C5,C^-}$ = 90,9[i] 159,9[r] | -116,6 (CN) 119,1 (CN) 165,1 (CO) 47,6 ($C^-$) 119,0[r] (CN) 165,0[r] (CO) 47,5[r] ($C^-$) | DMSO-d6 | [33] |
| $Ar^s$ | | | | | 153,6...158,3 | | Chloroform-d1 | [11] |

TABLE 3 (continued)

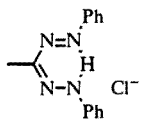
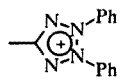
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| $C^-(N{=}NPh)_2$ | -130,5 | -27,5 | -91,3 | -73,2 | | 75,7 (N)<br>2,4 (NPh) | DMSO-$d_6$ | [40] |
|  | -139,9 | -25,9 | -93.9 | -79,3 | | 21,6 (N)<br>-49,2 (NPh) | DMSO-$d_6$ | [40] |
|  <br>2 $Cl^-$ | -132,3 | -20,5 | -89,7 | -70,4 | 149,8 | -56,9 (N)<br>-95,6 (NPh)<br>145,9 ($C^-$) | DMSO-$d_6$ | [40] |
| | | | | Y = NPh, $R^3$ = Et | | | | |
| $S^-$ | | | | | 175,5 | | DMSO-$d_6$ | [5] |
| $Se^-$ | | | | | 165,8 | | DMSO-$d_6$ | [5] |
| | | | | Y = NMe, $R^3$ = Me | | | | |
| $N^-H$ | -178,5 | -43,3 | -177,6<br>(350) | -116,5 | 162,5 | -271,2 (N)<br>(660) | DMSO-$d_6$ | [35] |
| $NH_2/Cl^-$ | -179,1 | -30,6 | -109,0<br>(1100) | -107,4 | 158,1[c] | -320,9 (N)<br>$^1J_{NH}$ = 89,6 Hz | DMSO-$d_6$ | [35] |
| $O^-$ | -178,4<br>(814) | -39,3<br>(1100) | -117,7<br>(260) | -113,5 | 161,1[c] | | DMSO-$d_6$ | [35] |
| $S^-$ | -148,2 | -26,6 | -107,9 | -74,8 | 173,9 | | DMSO-$d_6$ | [35] |
| $SMe/Cl^-$ | -148,6 | -16,5 | -100,9 | -71,1 | 162,4 | | DMSO-$d_6$ | [35] |
| | | | | | | | DMSO-$d_6$ | [35] |
| | | | | Y = NH, $R^3$ = Ph | | | | |
| $NH_2/CF_3COO^-$ | -178,9<br>(860) | -30,3 | -105,7<br>(370) | -108,4 | 160,6 | -333,5 (N) | TFA-$d_1$ | [35] |

TABLE 3 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| SMe/$CF_3COO^-$ | -111 | -11,6 | -101,1 (660) | -79,5 | 167,6 | | TFA-$d_1$ | [35] |

[a] $^{17}O$ NMR chemical shifts (ppm) with respect to $H_2O$ signal (0 ppm) and signal half-width (Hz) in parenthesis.

[b] $^{15}N$ NMR chemical shifts (ppm) with respect to $CH_3NO_2$ signal (0 ppm) and $^{14}N$ signal half-width (Hz) in parenthesis.

[c] $^{13}C$ NMR chemical shifts with respect to $(CH_3)_4Si$ signal (0 ppm).

[d] Abbreviations: DMSO — dimethylsulfoxide; TFA — trifluoroacetic acid.

[e] Multiplet on the fully coupled $^{13}C$ NMR spectrum; coupling with protons of the exocyclic group ~1.9-7.1 Hz.

[f] Unstable compound. Measurement taken on acetone-$d_6$ solution by $^{14}N$ NMR technique. $^{14}N$ NMR chemical shift (ppm) and signal halfwidth (Hz) is given.

[g] Measurement at 353 K for solubility increasing.

[h] $^{15}N$ labeled compound was used.

[i] $^1JC5\text{-}C^-$ coupling constant (Hz), measurement taken on a DMSO-$d_6$ solution, see Ref. 36, 37 for details.

[j] Hindered rotation of exocyclic group.

[k] Only one CN signal was found, due to signal superposition.

[l] Multiplet on the fully coupled $^{15}N$ NMR spectrum; coupling with protons of the side groups ~1.3-2.6 Hz.

[m] $C^-$ signal not found due to signal superposition.

[n] $^1JC5\text{-}C^-$ coupling constant (Hz), measurement taken on an $CDCl_3$ solution, see Ref. 36, 37 for details.

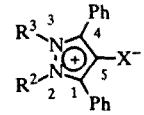
[o] Chloroform-$d_1$, solution, Ref. 15.

[p] $^{14}N$ NMR signal linewidth (Hz); measurement taken on an acetone-$d_6$ solution.

[r] DMSO-$d_6$ solution, Ref. 15.

[s] Various aromatic exocyclic groups, derivatives of cyclopentadiene ring.

TABLE 4. NMR Spectral Parameters of Some Type B Mesoionic Compounds, Derivatives of Pyrazole



| $X^-$ | N2(N3)[a] | Cl(C4)[b] | C5[b] | Ref. |
|---|---|---|---|---|
| | **$R^2$ = $R^3$ = Me** | | | [24] |
| $O^-$ | -215,6 | 136,9 | 151,9 | |
| | -207,5[c] | 138,2[c] | 147,9[c] | |
| | -208,4[d] | 138,0[d] | 149,2[d] | |
| | -200,9[e] | 140,3[e] | 138,1[e] | |
| | -199,7[f] | 139,0[f] | 137,5[f] | |
| OMe/$I^-$ | -199,1 | 139,5 | 140,3[g] | |
| $OCH_2Ph/Cl^-$ | -197,9 | 141,1 | 138,9[g] | |
| | **$R^2$ = Me, $R^3$ = Ph** | | | |
| $O^-$ | -205,4 NMe | 139,7 Cl[h] | 143,4 | |
| | -193,2 NPh | 136,3 C4[h] | 140,0[f] | |
| | -201,7 NMe[d] | 138,4 Cl[f,h] | | |
| | -190,5 NPh[d] | 136,3 C4[f,h] | | |
| | -198,1 NMe[f] | | | |
| | -187,9 NPh[f] | | | |

All measurements were taken on a $CDCl_3$ solution, if not specified to the contrary.

[a] $^{15}N$ NMR chemical shift (ppm) with respect to $CH_3NO_2$ signal (0 ppm).

[b] $^{13}C$ NMR chemical shifts with respect to $(CH_3)_4Si$ signal (0 ppm).

[c] Measurement taken on a $D_2O$ solution.

[d] Measurement taken on a $CD_3OD$ solution.

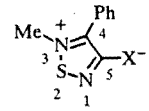
[e] Measurement taken on a $D_2O$/HCl solution.

[f] Measurement taken on a $CD_3OD$/HCl solution.

[g] Couplings of C5 atom with protons of exocyclic group on the fully coupled $^{13}C$ NMR spectra, 3.1-4.1 Hz.

[h] The assignment can be reversed.

TABLE 5. The NMR Spectral Parameters of Some Mesoionic 2,1,3-Thiadiazoles of Type B



| $X^-$ | N1[a] | N3[a] | C4[b] | C5[b] | Ref. |
|---|---|---|---|---|---|
| $O^-$ | -154,8 | -150,7 (360) | 149,2 | 165,4 | [34] |
| $OH/Cl^-$ | -117,9 | -138,5 (760) | 149,2 | 159,6 | |
| $OEt/BF_4^-$ | -115,1 | -136,0 (700) | 149,8 | 158,5[c] | |

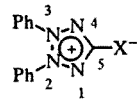
All measurements were taken on a DMSO-$d_6$ solution.

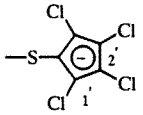
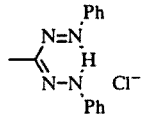
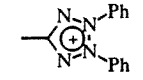
[a] $^{15}N$ NMR chemical shift (ppm) with respect to $CH_3NO_2$ signal (0 ppm) and $^{14}N$ signal half-with (Hz) in parenthesis.

[b] $^{13}C$ NMR chemical shift with respect to $(CH_3)_4Si$ signal (0 ppm).

[c] Coupling constant (Hz) of C5 atom with methylene protons of exocyclic group, $^3J_{C5,C\underline{H}_2}$

TABLE 6. The NMR Spectral Paramters of Mesoionic Tetrazoles of Type B

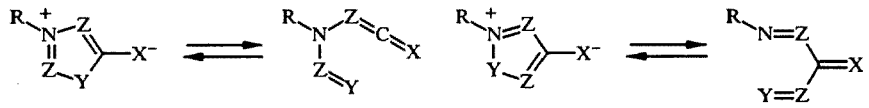


| $X^-$ | N1(N4)[a] | N2(N3)[a] | C5[b] | 5-exo[a,b] | Ref. |
|---|---|---|---|---|---|
| $O^-$ | -97,9 | -119,5 | 169,7<br>169,6[c] | | [20] |
| $OEt/BF_4^-$ | -94,0 | -108,0 | 168,4[d] | | [20] |
| $S^-$ | -64,5 | -108,5 | 181,4 | | [20] |
| $SMe/BF_4^-$ | -67,8 | -100,1 | 167,6d | | [20] |
| $C^-(CN)_2$ | -89,0 | -106,8 | 169,2[e]<br>169,2[g] | -116,3(CN); 119,7 (CN); 22,6 ($C^-$); 112,7[f] (CN); 22,9[f] ($C^-$); 119,6[g] (CN); 22,4[g] ($C^-$) | [30] |
| $C^-(CN)(COOEt)$ | -84,0<br>-58,9[f] | -108,4<br>-98,0[f] | 168,3[h] | -120,3(CN); 121,9 (CN); 165,8 (CO); 47,8 ($C^-$); -131,4[f] (CN); 109,0[f] (CN); 158,6[f] (CO); 36,0[f,i] ($C^-$) | [30] |
| $S—C^-(CN)_2$ | -68,6<br>-65,5[f] | -99,5<br>-97,6[f] | 171,0<br>164,6[f]<br>171,1[j] | -129,5 (CN); 124,9 (CN); 4,3 ($C^-$); -128,9[f] (CN); 110,6[f] (CN); 23,4[f] ($C^-$); 125,2[j] (CN); 4,5[j] ($C^-$) | [30] |
|  | | | 169,4 | 105,3, 100,2 (C1', C2') | [14] |
| $S—C^-(CN)(COOEt)$[k] | -66,6 | -98,6 | 164,3[l] | -136,3 (CN); 112,0[m] (CN); 162,7 (CO); 37,1[m] ($C^-$) | [30] |
| $N^-Ts$ | -89,6<br>-88,7f | -109,9<br>-105,5[f] | 165,3<br>158,6[f] | -233,7; -266,2[f] | [29] |
| $(—N—N=O)^-$ | -90,0<br>-75,3n | -108,2<br>-101,8[n] | 174,1<br>165,6[n] | 241,7, -41,4 (N—N=O); 145,9, -14,0 (N=N—OH)[n] | [29] |
| —N=N—OMe/$I^-$ | -73,6 | -100,3 | 163,5 | 136,6, -5,2 (N=N—OMe); 62,6 (Me) | [29] |
| $NH_2/Cl^-$ | -100,8 | -111,1 | 165,3 | -326,1 (N); $^1J_{NH}$ = 88 Hz | [29] |
| —Ph/$Cl^-$ | -68,3 | -100,3 | 163,9 | | [30] |
| | -66,2 | -101,0 | 161,2 | 17,5 (N); -51,5 (NPh); 131,2 (C) | [40] |
|  | -60,3 | -95,9 | 152,2 | -60,3 (N); -95,9 (NPh); 152,2 (C) | [40] |
|  2 $Cl^-$ | | | | | |

All measurements were taken on a DMSO-$d_6$ solution, if not specified contrary. [a] $^{15}N$ NMR chemical shift (ppm) with respect to $CH_3NO_2$ signal (0 ppm). [b] $^{13}C$ NMR chemical shift with respect to $(CH_3)_4Si$ signal (0 ppm). [c] Ref. 15. [d] Coupling constant (Hz) of C5 atom with protons of exocyclic alkyl group, ~3.0-5.4 Hz. [e] $^{13}C$-$^{13}C$ coupling constant; $^1JC5\text{-}C^-$ = 96.1 Hz, $^1J_{C^-,\,CN}$ = 98.5 Hz. Ref. 36. [f] Measurement taken on a trifluoroacetic acid (TFA) solution. [g] Ref. 15. [h] $^{13}C$-$^{13}C$ coupling constant; $^1J_{C5,C-}$ = 92.5 Hz for free compound (DMSO-$d_6$ solution); [i] $^1J_{C5,C^-}$ = 59.6 Hz and $^1J_{C-CO}$ = 65.8 Hz for protonated compound (TFA solution). Ref. 36. Coupling constant with proton attached to $C^-$ atom, $^1J_{C\text{-}H}$ = 141.4 Hz. [j] Ref. 14. [k] Measurement taken in TFA solution; isomerisation of compound to nonmesoionic form occurs in DMSO solution. [l] Coupling constant (Hz) of C5 atom with proton attached to $C^-$ atom, $^3J$ = 7.4 Hz (TFA solution). [m] Coupling constant (Hz) with proton attached to $C^-$ atom, $^2J_{CN,H}$ = 10.9 Hz, $^1J_{C\text{-}H}$ = 148.7 Hz; TFA solution. [n] DMSO-$d_6$ solution with addition of hydrochloric acid (protonated exocyclic group).

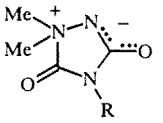
of these compounds may not be clear. Some experimental data suggest that an open chain isomer plays an important part in various reactions (Scheme 2). Thus, despite x-ray data that confirm the existence of the ring mesoionic structure in the solid state, the presence of a linear isomer in solution may occur.

Scheme 2



The valence tautomerism of mesoionic compounds

There are NMR spectral data for mesoionic compounds of type A derivatives of: oxazole [3, 18], 1-oxa-2,3-diazole [1, 4, 6-10, 12, 13, 15, 17, 18, 21, 22, 25] (Table 1), 1-thia-2,3-diazole [27] (Table 1), 1,2,3-triazole [16] (Table 1), 1-thia-3,4-diazole [32] (Table 2), 1,3,4-triazole [32, 42, 43] (Table 2), 1-oxa-2,3,4-triazole [19, 25, 26, 39, 44] (Table 3), 1-thia-2,3,4-triazole [19, 26, 31, 37, 39] (Table 3) and tetrazole [5, 11, 14, 15, 25, 33, 35, 36, 40] (Table 3), also for the compounds of type B, such as derivatives of pirazole [24, 38] (Table 4), 1-thia-2,5-diazole [34] (Table 5) and tetrazole [14, 15, 20, 25, 28, 29, 30, 36, 40, 41] (Table 6). An example of other class of dipolar compounds is given for comparison purposes in [23].



The analogous group of compounds [23]

Most papers refereed into the present work regard $^{15}N$ NMR spectral data of mesoionic structures. Typically, samples with a natural abundance of $^{15}N$ were used for the measurements. However some $^{15}N$ labeled structures were synthesized and employed. The quite difficult question of $^{15}N$ NMR signal assignment is worthy of attention. Various techniques are available in modern NMR spectroscopy for solving those problems:

— $^{15}N$ NMR measurements by INVGATE and INEPT technique.
— Two-dimensional correlation techniques, such as $^{1}H$-$^{15}N$ COLOC, $^{1}H$-$^{13}C$ HETCOR.
— Detection of coupling constants by the INADEQUATE technique.
— Selective heterodecoupling.
— Detection of the NOE effect.

In some cases *ab initio* molecular orbital calculations of nuclear screening constants [25] and $^{15}N$ labeling was used for signal assignment purposes. An elaboration concerning the use of NMR spectral data has been missing until now. Thus, this part of the work is interesting in itself and useful for further applications.

Conclusions concerning molecular structures are based on NMR spectral parameters. The data exhibit a large similarity of nitrogen chemical shifts for the mesoionic compounds investigated and its protonated form. A protonated mesoionic structure can be regard as a derivative of an azolium cation. Consequently, the NMR data suggest the similarity of an aromatic ring for those two forms. The x-ray data and CP-MAS data lead to similar conclusions for the solid state of the compounds studied. Thus, the mesoionic compounds can be considered as an azolium cation with a negative substituent at the 5 position, and the total electric charge in the molecule is equal to zero.

Generally, NMR signals of the open-chain form (Scheme 2) of mesoionic heterocycles are not observed in the recorded spectra. The $^{15}N$ NMR chemical shifts of the open chain form should be drastically different from those observed for the diazo-

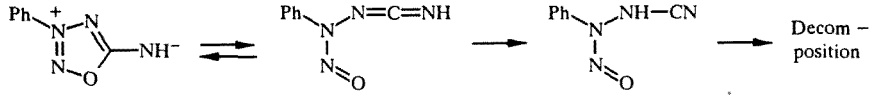
Scheme 3

observed structure

The possible isomeric structures of 2,2'-dipyridylketone

lium cation form of the investigated compounds. Of course, the presence of a small concentration of a linear tautomer in equilibrium with the corresponding cyclic mesoionic structure is possible. However, a significant concentration of the linear form is excluded. Another example is that of 2,2'-dipirydylketone (Scheme 3, Ref. 38), which can be considered as a linear form of the corresponding mesoionic structure. Our proposed rearrangement scheme of the mesoionic derivative of 1-oxa-2,3,4-triazole to its linear structure (Scheme 4, Ref. 44) is also an interesting case.

Scheme 4

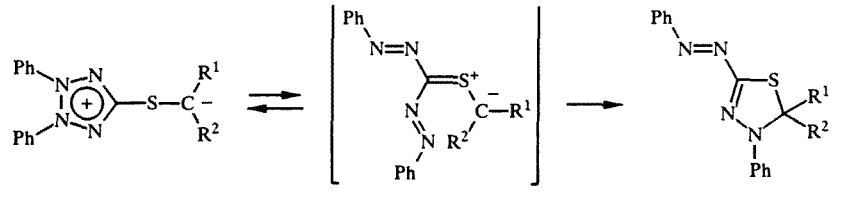



The rearrangement scheme for mesoionic compound of type A

An estimation of the charge density distribution in a molecule is another important application of the $^{14}N$ NMR technique. The interpretation of quadrupolar relaxation of a $^{14}N$ nucleus and the resulting half line width of its NMR signal provides information on the positive charge density distribution in a molecule. The comparison is rationalized, for consideration of different nitrogen atoms in a given molecule, provided that the rotational anisotropy of the molecule is insignificant. Generally, a narrow $^{14}N$ NMR signal suggests a positive charge excess on the nucleus of interest. This method is used in our various reports of positive charge distribution in mesoionic aromatic rings, for both types A and B compounds. The results lead us to some conclusions that are helpful for understanding the real structure of mesoionic species.

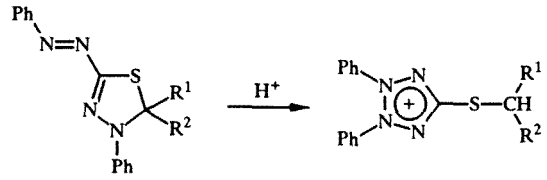
A protonation process of a mesoionic molecule and salt formation, is an other interesting part of the work. In principle protonation may occur either on an exocyclic group or on an atom in the mesoionic ring. Large difference in the $^{15}N$ chemical shifts for mesoionic compounds, before and after protonation, is the probe for structural studies. The protonation of an exocyclic nitrogen atom in mesoionic aminides results in a large increase in shielding of its $^{15}N$ signal. Such effects are observed for all compounds investigated. A similar, but weaker effect is observed for the C6 atom in $^{13}C$ NMR. Isomerization of a mesoionic tetrazole with an exocyclic group extended by a sulphur atom (Scheme 5, Ref. 30) is an interesting case. The compound exists in the mesoionic form (formally as an azolium cation) only in acidic conditions; protonation occurs on an exocyclic carbon atom. On the contrary, the compound assumes a non-mesoionic form in neutral conditions (Scheme 6).

Scheme 5



The rearrangement scheme for mesoionic compound of type B

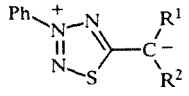
Scheme 6



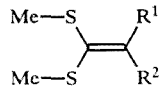
The pH dependence of a given mesoionic structure

Our investigations lead to the conclusion that the protonation of the mesoionic structure occurs on the exocyclic group. Consequently, the dipolar structure of mesoionic compounds, with a formal positive charge in the ring and a negative charge on the exocyclic group is evident.

The character of an exocyclic bond has been subject of supplementary investigations. Our observations suggest that the bond has partially double bond properties. The $^{13}C$ NMR chemical shifts, typical for double bonds are the proof. The one bond coupling constant $^{1}J_{C5\text{-}C6}$ or $^{1}J_{C5\text{-}Se6}$ is the additional, quite interesting evidence. We have observed [37] that the C5-C6 coupling constants for derivatives of 1-thia-2,3,4-triazole are similar to those observed for the model compounds containing a double bond.

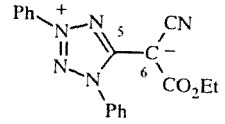


where : $R^1$, $R^2$ = CN, $CO_2Et$, COMe, COEt, COPh, CONHPh;
$^{1}J_{C5,C6}$ = 71,1 - 92,7 Hz

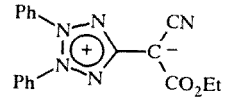


where : $R^1$, $R^2$ = CN, $CO_2Et$;
$^{1}J_{C5,C6}$ = 78,4 - 83,3 Hz

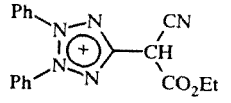
Analogous results are obtained for derivatives of mesoionic tetrazoles of both types A and B.



$^{1}J_{C5-C6}$ 90,9 Hz



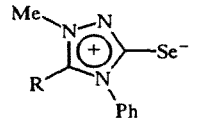
92,5 Hz



59,6 Hz

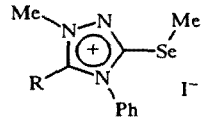
$CF_3CO_2^-$

The magnitude of $^{1}J(^{77}Se\text{-}^{13}C)$ couplings [43], and the restricted rotation of the exocyclic group in derivatives of 1-thia-2,3,4-triazole [31, 37, 39], are other proofs.



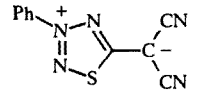
R = Me, Ph

$^1J_{^{77}Se-^{13}C5}$ = 228 Hz



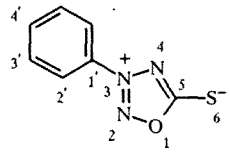
$^1J_{^{77}Se-^{13}C5}$ = 164 Hz

$^1J_{^{77}Se-^{13}Me}$ = 56 Hz



| | $^{15}$N NMR | $^{13}$C NMR |
|---|---|---|
| | − 113,4 ppm | 117,0 ppm |
| | − 108,1 ppm | 114,5 ppm |

Comparison of mesoionic structure in solution and in the solid state seems to be quite an interesting question. Measurements in the solid state have been made by the $^{15}$N and $^{13}$C NMR CP MAS technique (i.e., cross polarization and magic angle sample spinning). The $^{15}$N and $^{13}$C chemical shifts for the derivatives of 1-thia-2,3,4-triazole and 1-oxa-2,3,4-triazole are similar for the solid and solution states [39]. The data for the latter compounds are given below.



| | Solid state | DMSO solution |
|---|---|---|
| N2 | 11,8 | 12,9 |
| N3 | − 63,7 | − 64,5 |
| N4 | − 110,2 | − 107,5 |
| C5 | 192,5 | 191,8 |
| C1' | 136,7 | 133,2 |
| C2' | 119,4 | 122,0 |
| C3' | 124,1 | 130,4 |
| C4' | 133,4 | 134,4 |

Restricted rotation of the exocyclic group around the C5-C6 bond for 1-thia-2,3,4-triazolomethylides is observed in the solution as well as in the solid state. The results obtained lead us to the important conclusion that the cyclic mesoionic structures found in solution exist also in the solid state in the same structure.

$^1$H NMR data concerning mesoionic compounds are given in many papers. The $^1$H NMR technique has been used for the identification and purity determination rather than for structural investigation, thus, those papers are not included in the present work. All reported NMR data concerning the structural study of these classes of compounds are given in Tables 1-6.

The most useful and sensitive NMR spectral parameters have been applied to the unambiguous identification of mesoionic compounds, their isomers and valence tautomers. We hope that the utilization of the various NMR methods is clearly shown. In particular, the specific properties of the $^{14}$N and $^{15}$N nuclei are useful for structural studies. Most of the measurements concerning nitrogen NMR have been performed by our group of co-workers.

Mesoionic compounds exhibit high biological activity and they are the subject of attention from various branches of science. These compounds find application in pharmacy, agriculture, technology of photographic materials, and for the construction of modern galvanic cells. In addition, mesoionic compounds are useful substrates in organic syntheses. The structural study of this group of compounds is certainly rational and of potential in many areas of science and technology.

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