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Graphical Abstract

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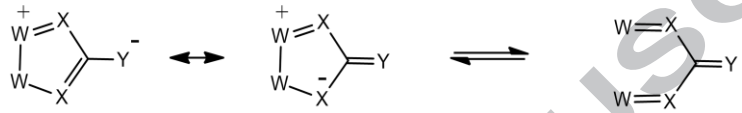

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ABSTRACT

The MP2 calculated Gibbs free energies of a series of type B mesoionic rings and their acyclic valence tautomers suggest that in the gas phase the relative stability of the mesoionic ring increases with single bond strength (S-S > RN-NR > O-O). Inclusion of aqueous solvation in the calculations further favours the stability of the mesoionic ring by ~10-15 kcal mol^{-1}. Replacement of CR groups at ring positions by nitrogen atoms results in a significant increase in the relative stability of the mesoionic ring. Calculations of aromatic stabilization energy (ASE), together with the Bird aromaticity index (I_5), suggest that aromaticity decreases with aza substitution and the increase in relative stability is attributable to charge stabilisation by the electronegative nitrogen atoms, which more than compensates for any loss of aromaticity.

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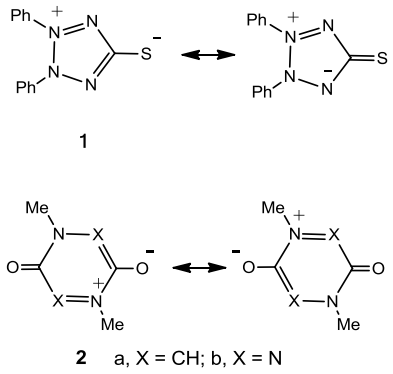
1. Introduction

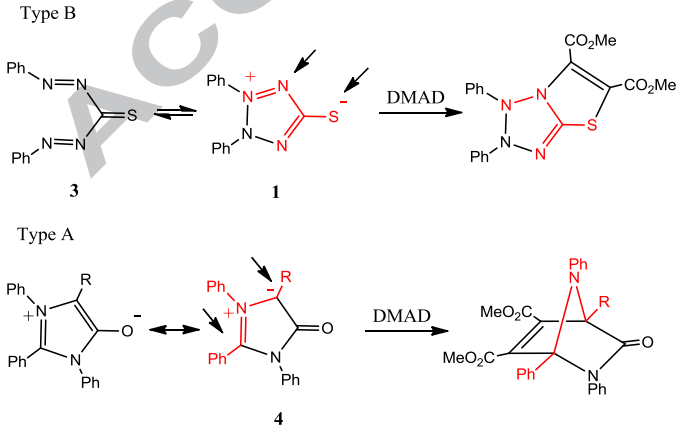
Type B mesoionic rings, exemplified by dehydrodithizone **1**, have recently been reclassified as semi-conjugated mesomeric betaines.[1,2] They are structurally related to the tetrazinium-3-olate **2b**,[3] which, as far as we are aware, is the only other known example of a semi-conjugated mesomeric betaine. The structures and properties of this relatively unexplored general class of dipolar heterocycles are of some interest.



Examples of semi-conjugated mesomeric betaines.[1]

Three main classes of heterocyclic mesomeric betaine are now recognised: conjugated (Class 1), cross-conjugated (Class 2) and semi-conjugated (Class 3).[1]

Type A and type B mesoionic heterocycles are isoconjugate isomeric ring systems that differ in the positions of the two heteroatoms (O, S or NR) that each formally contribute two π electrons to the bonding.[4-6] Type A mesoionic rings, e.g., 1,3-diazolium-4-olates **4**, are conjugated mesomeric betaines and their 1,3-dipolar cycloaddition reactions are well known.[4-6] Type B mesoionic rings, e.g., 1,2,3,5-tetrazolium-4-thiolates **1**, were previously classified as conjugated,[6] but this is now considered to be incorrect.[1] They do undergo cycloaddition reactions, as illustrated in Scheme 1,[7] but the dipolar ring fragment associated with the addition (**1**; Scheme 1) is quite distinct from that associated with type A cycloadditions, illustrated by the 1,3-dipolar cycloadditions of 1,3-diazolium-4-olates (**4**; Scheme 1).[8] In each case the initial adducts are intermediates leading to further products.



Scheme 1. Examples of cycloadditions of type A and type B mesoionic rings.

Another possible mode of reaction of type B mesoionic heterocycles is ring opening to an acyclic valence tautomer, e.g., **1** → **3**.[4-6] We now report a DFT and *ab initio* study of the effect of ring modification on the structure and stability of type B mesoionic rings and the factors determining the position of equilibrium between type B rings and their valence tautomers, e.g., **1** and **3**.

2. Computational details

All calculations were performed by using Gaussian 16 software.[9] Two models were employed: *ab initio* MP2[10] with the Dunning correlation-consistent aug-cc-pVDZ basis set[11,12] and density functional B3LYP[13,14] with the Pople 6-311++G(d,p) basis set.[15] Full geometry optimizations were performed for the gas phase and for the water environment modelled by the IEFPCM continuum model,[16] and followed by frequency calculations to obtain the Gibbs free energy corrections and ensure that the obtained minima are true minima on the potential energy surface. Natural Bond Analysis was performed by the NBO 6.0 program[17] interfaced to Gaussian. Then, the pEDA index was calculated using the freely available AromaTcl software.[18] The discussion of the energetics of studied molecules was generally performed in relation to Gibbs free energy; only for the homodesmotic reactions were E+ZPE (Total Energy + Zero Point Correction) values used to allow comparisons with previous works.

3. Results and Discussion

To investigate the influence of structural features on valence tautomerism we have calculated the Gibbs free energy differences between fifteen symmetrical cyclic structures **5** and their acyclic isomers **6** using the *ab initio* MP2 method. We have also calculated water-solvated free energies using the PCM (Polarised Continuum Model) method which simulates the averaged environmental solvation by water. The Gibbs free energies (E + ZPE) and free energy differences (ΔG) for both gas phase (ΔG_{GP}) and solvated species ($\Delta G_{SOLVATED}$) are shown in Table 1.

The free energy differences (ΔG: kcal mol^{-1}) between the isomers **5** and **6** are of some interest. There is a clear trend in the series W = O, NR, S (Entries 1-5) where the stability of the cyclic form correlates with increasing single bond strength (S-S > RN-NR > O-O). Tricarbonyl structures **6** (e.g., W = Y = O, X = CMe) (Entry 1) are much more stable than the cyclic form **5**. This is not unexpected and entirely consistent with a study of the chemistry and crystal structures of propane-1,2,3-triones, which showed no evidence of equilibration with the mesoionic form.[19] In contrast, 1,2-dithiolium-4-olates (e.g., Entry 5) are known to exist as the cyclic form and the structure of the 3,5-diphenyl derivative has been confirmed by X-ray crystallography.[19,20] The calculated energies between the valence tautomers in Entry 5 are consistent with the observed relative stability; there is no published evidence that these molecules react *via* the acyclic tautomers **6** (W = S, X= CR, Y = O).[21]

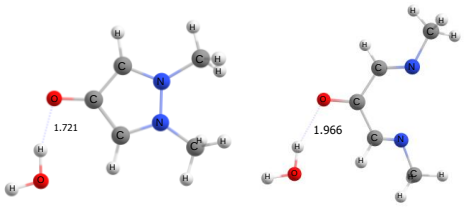
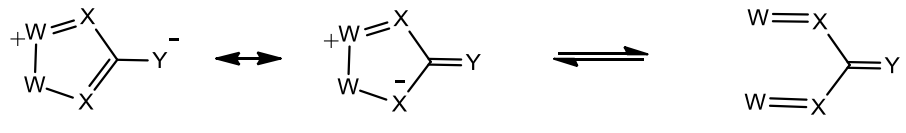


Figure 1. MP2 calculated gas phase monohydration of 1,2-dimethyl-1,2-diazolium- 4-olate and its valence tautomer.

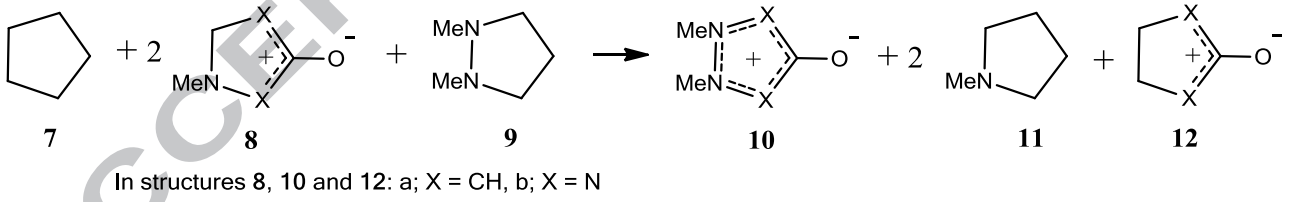
Table 1. MP2 calculated properties of valence tautomers **5** and **6**.



5 **6**

Entry	W	X	Y	Gas phase E+ZPE[a]			Solvated E+ZPE[a]		
				5	**6**	ΔG_{GP}[b]	**5**	**6**	$\Delta G_{SOLVATED}$[b]
1	O	CMe	O	-418.5350910	-418.659351	77.97	-418.549223	-418.668285	74.71
2a	NPh	CMe	O	-839.497758	-839.515675	11.24	-839.522137	-839.525608	2.18
2b	NPh	CMe	O + 1H_2O	-915.759420	-915.769087	6.07	-915.785792	-915.782343	-2.16
3	NMe	CMe	O	-457.207519	-457.226667	12.02	-457.236243	-457.235632	-0.38
4a	NMe	CH	O	-378.865033	-378.887225	13.93	-378.896355	-378.896069	-0.18
4b	NMe	CH	O + 1H_2O	-455.127190	-455.140241	8.19	-455.161045	-455.153566	-4.69
5	S	CMe	O	-1063.867307	-1063.861143	-3.87	-1063.879460	-1063.866290	-8.26
6	NPh	N	O	-793.227337	-793.200720	-16.70	-793.252707	-793.208322	-27.85
7	NMe	N	O	-410.946192	-410.918737	-17.23	-410.977298	-410.927390	-31.32
8	NPh	N	S	-1115.825607	-1115.796925	-18.00	-1115.856430	-1115.805280	-32.10
9	NMe	N	S	-733.544540	-733.515117	-18.46	-733.582949	-733.521975	-38.26
10	NPh	N	NNO	-902.358936	-902.330419	-17.89	-902.396905	-902.339817	-35.82
11	NMe	N	NNO	-520.078000	-520.047554	-19.11	-520.122407	-520.055092	-42.24
12	S	N	O	-1017.610855	-1017.529572	-51.01	-1017.624260	-1017.536300	-55.20
13	S	N	S	-1340.201726	-1340.129458	-45.35	-1340.219350	-1340.134390	-53.31
14	O	N	O	-372.329927	-372.241282	-55.63	-372.330671	-372.245669	-53.34
15	O	N	S	-694.911433	-694.840524	-44.50	-694.910699	-694.843475	-42.18

[a]Hartrees, [b]kcal mol^{-1}



7 **8** **9** **10** **11** **12**

In structures 8, 10 and 12: a; X = CH, b; X = N

Figure 2. Homodesmotic schemes used to calculate the aromatic stabilisation energies (ASEs) shown in Table 3.

The case of the 1,2-diazolium-4-olates (Entries 2-4) is less clear. A number of these derivatives have been reported and they exist in the cyclic form **5** (W = NR, X = CR, Y = O).[22] The results in Table 1 suggest that in the gas phase the ring-open form **6** (W = NR, X = CR, Y = O) is more stable. However, solvation appears to stabilise the cyclic form by 12 ± 3 kcal mol^{-1} (Table 1). In view of the polarity of type B mesoionic rings, this solvation effect is not surprising. Some of the known 1,2-diazolium-4-olates are characterised as hydrates.[22] Studies of their chemistry are limited but there is no evidence of reactions *via* the acyclic tautomer. Inclusion of a specific water molecule in the calculation (Entries 2b and 4b) leads to a further relative stabilisation of the ring (*ca.* 5 kcal mol^{-1}). Figure 1 shows the calculated gas phase monohydrated forms of the isomers **5** and **6** (W = NMe, X = CH, Y = O) (Entry 4b). Both water molecules are hydrogen bonded to the carbonyl oxygen but bonding to the mesoionic isomer **5** (H⋯O, 1.721 Å) is stronger than that in the isomer **6** (H⋯O, 1.721 Å). Solvation and intermolecular bonds probably play a role in stabilising the 1,2-diazolium-4-olate ring, and other type B rings.

Aza substitution at positions 3 and 5 (**5**; X = N) considerably increases the relative stability of the mesoionic isomers **5** (Table 1, Entries 6-15). In all cases the mesoionic isomer **5** is significantly more stable than the valence tautomer **6**, even in the gas phase. It might be assumed that this is because the aza derivatives (**5**; X = N) are more aromatic than the parent rings (5; X = CR) but this does not seem to be the case. Aromaticity appears to decrease with aza substitution. Inspection of Table 3

shows that the Bird aromaticity index (I_5) [23] decreases as the gas phase relative stability increases.

We have estimated the aromatic stabilisation energies (ASEs) of the 1,2-diazolium-4-olate (**10a**) and the 1,2,3,4-tetrazolium-5-olate (**10b**) using the homodesmotic equations shown in Figure 2. We have previously calculated the ASE of ring **10a** using an alternative homodesmotic equation.[24] An advantageous feature of the equations shown in Figure 2 is that all structures retain the symmetry of the dipolar elements. In order to be able to make a direct comparison with our earlier results, the energies of the species **7**-**12** (Figure 2) were calculated by both the MP2 and B3LYP methods.

Table 2. Gas-phase optimised energies[a] including ZPE of structures **7**-**12**.

Ring	E + ZPE (MP2)	E + ZPE (B3LYP)
7	-195.782029	-196.471753
8a	-323.640390	-324.629980
8b	-355.707510	-356.724200
9	-306.068293	-307.080091
10a	-378.832040	-379.968400
10b	-410.912980	-412.070540
11	-250.966140	-251.809860
12a	-268.419180	-269.254740
12b	-300.466780	-301.328030

[a]Hartrees

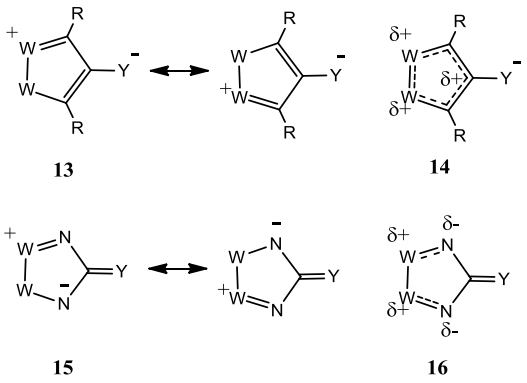
The gas phase optimised energies including zero-point vibrational correction (ZPE) of structures **7**-**12** (X = CH, N) are shown in Table 2. To avoid the inclusion of σ-bonding effects and associated distortions, the geometries of the contributing functional groups were restrained to those in the target molecules **10**. This restricts the evaluation to π effects and gives an estimate of the additional stabilisation attributable to π cyclic conjugation. Both computational methods indicate that the ASE (Table 3) decreases with aza substitution, in agreement with the Bird index (I_5). The ASEs obtained using MP2 are greater than those using B3LYP but the trends are the same using both methods. The B3LYP calculated ASE for **10a** (19.5 kcal mol^{-1}) (Table 3, Entry 1) is in good agreement with the value we obtained previously (15.8 kcal mol^{-1}) using an alternative homodesmotic equation.[24] We have previously calculated the ASE of the semi-conjugated ring **2b** and found that the ASE (6.5 kcal mol^{-1}) is also less than that of the corresponding deaza derivative **2a** (18.1 kcal mol^{-1}).[25]

It is clear that the extra relative stabilisation of the aza-substituted type B molecules cannot be attributed to an increase in aromaticity. The stabilisation probably arises from greater stabilisation of negative charge due to the electronegative nitrogen atoms.

In the deaza derivatives **10** (X = CR) resonance structures with the negative charge on the exocyclic atom, e.g., **13**, probably make a significant contribution to the structure, with the overall structure being polarised in a manner similar to that shown in general structure **14**. In the aza derivatives **10** (X = N) the electronegative nitrogen atoms attract more negative charge to the ring and resonance structures of the type **15** have more significance. In this case general structures of the type **16** may make a greater contribution to the structure. This view is supported by the observation that calculated exocyclic CO bond lengths in the aza derivatives are significantly shorter (Table 3, Entries 4,5) than those of the deaza derivatives (Table 3, Entries 1-3). X-ray data on type B mesoionic rings is limited but the gas phase calculated bond lengths are in reasonable agreement with the crystal structure values shown in Table 3. The CO bond lengths in the aza derivatives (Entries 4,5), although shorter than in the deaza derivatives (Entries 1-3), are still of comparable length to those in amides (1.2-1.3 Å) suggesting that resonance structures with exocyclic charge still contribute.

The calculated pEDA values (Table 3) are also consistent with the generalised structures **14** and **16**. The index pEDA is the sum of the populations of the ring p_z atomic orbitals, calculated by the NBO (Natural Bond Orbital) method,[17] minus the aromatic sextet value of six.[26] The resulting number shows how much the ring is π-excessive (positive number) or π-deficient (negative number). In the case of the type-B mesoionic compounds shown in Table 3, pEDA varies between 1.07 and 1.318. These type B rings are all electron rich (pEDA > 0) but the aza derivatives show a significant increase in ring π electrons (Table 3) and are thus less aromatic. Similar trends in bond length[27] and pEDA are seen for the dithia derivatives shown in Table 3 (Entries 6-7).

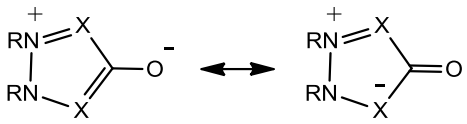
Due to the ring aza effect, the tetrazoles **5** (W = NR, X = N) are all significantly more stable than their valence tautomers **6** (W = NR, X = N) (Table 1, Entries 6-11). The calculated energy differences (ΔG_{GP} and $\Delta G_{SOLVATED}$) suggest that the valence tautomers **6** may be thermally accessible. This is consistent with the experimental observation of reaction products of the derivatives **5** (W = NPh, X = N, Y = S, NNO) (Table 1, Entries 8 and 10) that can be rationalised by initial valence tautomerism (**5** → **6**).[4,12,28-32] The nature of the exocyclic group (Y = O, S, NNO) does not have a profound effect on relative stability. Interestingly, the tetrazolium-5-olate **5** (W = NPh, X = N, Y = O) has been known for over 120 years,[27,33,34] but no evidence of valence tautomerism has been reported for this molecule.



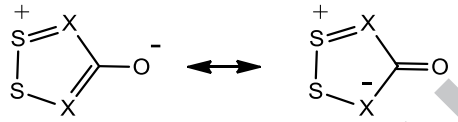
Resonance structures predominating for 3,5-deaza and 3,5-diaza type B mesoionic rings

The diaza derivatives of 1,2-dithiolium- and 1,2-dioxolium-4-olates and -thiolates (Table 1, Entries 12-15) are unknown, but are calculated to be much more stable (~40-55 kcal mol^{-1}) than the corresponding valence tautomers. In a previous study,[35] one of us investigated the preparation of 1,2,3,5-dithiadiazolium-4-thiolate **18** (Table 1, Entry 13) by S_N2 displacement of the mesoionic ring from a series of benzyl derivatives **17** using a variety of nucleophiles (Scheme 2). Although there was evidence of an S_N2 reaction, no evidence for formation of the desired product **18** was obtained. It was concluded that if formed the ring **18** rapidly underwent fragmentation.

Table 3. Properties of the type B mesoionic rings **5** (W = NR, Y = O) and **5** (W = S, Y = O).



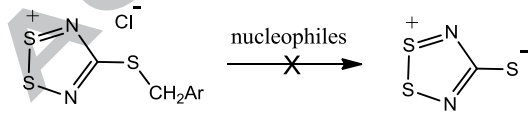
Entry	R	X	ΔG_{GP}[a]	I_5	ASE_{MP2} (ASE_{B3LYP})[a]	CO_{calc} (CO_{exp})[b]	NNcalc (NNexp)[b]	pEDA
1	Me	CH	13.93	94.4	32.9 (19.5)	1.255	1.350	1.166
2	Me	CMe	12.02	89.6	-	1.261	1.372	1.073
3	Ph	CMe	11.24	91.1	-	1.259	1.367	1.104
4	Me	N	-17.23	57.2	29.3 (11.3)	1.225	1.353	1.286
5	Ph	N	-16.70	56.5	-	1.223 (1.237)[c]	1.368 (1.326)[c]	1.274



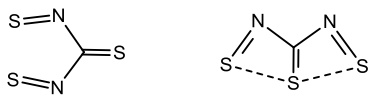
Entry	-	X	ΔG_{GP}[a]	I_5	-	-	CO_{calc} (CO_{exp})[b]	SScalc (SSexp)[b]	pEDA
6		CMe	-3.87	65.7			1.253	2.065	1.266
7		CPh	-	-			(1.250)[d]	(2.005)[d]	-
8		N	-51.01	-5.4			1.206	2.206	1.318

[a]kcal mol^{-1}, [b]Angstroms, [c]Ref. 27, [d]Ref. 19.

AM1 calculations[36] associated with the earlier study suggested that the mesoionic compound **18** corresponds to a local energy minimum and is more stable than the valence tautomer **19**.[35] Unexpectedly, it was calculated that a bicyclic structure **20** is more stable than the valence tautomer **19**. It is amusing to note that the MP2 method also finds that a similar bicyclic structure **20** corresponds to an energy minimum (E + ZPE -1340.161919 H) making it only 24.97 kcal mol^{-1} less stable than the mesoionic ring **18**. The AM1 and MP2 optimised structures have similar geometries as shown in Figure 3. Since formation of the species **20** presumably requires preliminary formation of the tautomer **19**, it seems unlikely that this molecule plays a role in the decomposition of the ring **18**.

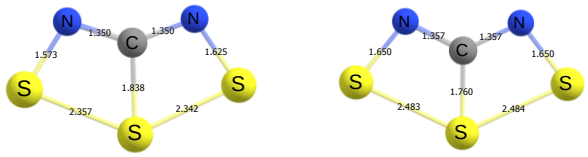


17 **18**



19 **20**

Scheme 2. 1,2,3,5-Dithiadiazolium-4-thiolate and its valence tautomers



(a) AM1 optimized [36] (b) MP2/aug-cc-pVDZ optimized

Figure 3. AM1 and MP2 optimised structures of isomer **20**.

4. Conclusions

We have calculated the properties of a series of type B mesoionic rings **5** and their ring-opened valence tautomers **6**. The calculated Gibbs free energies suggest that in the gas phase the relative stability of the mesoionic ring is favoured by the presence of an S-S bond and disfavoured by an O-O bond. Rings with an RN-NR bond have intermediate relative stability. Inclusion of the Polarised Continuum Model of aqueous solvation in the calculations favours the stability of the mesoionic ring by ~10-15 kcal mol^{-1} and this is consistent with the known stability of 1,2-dithiolium- and 1,2-diazolium-4-olates. Replacement of CR groups at the 3 and 4 ring positions by nitrogen atoms results in a significant increase in the relative stability of the mesoionic ring. This stabilisation is not due to an increase in aromaticity; calculations of aromatic stabilisation energies and the Bird aromaticity indexes (I_5) both suggest that thermodynamic aromaticity decreases with aza substitution. The pEDA index indicates that the number of ring π electron significantly increase above six with aza substitution and the increase in stability can be attributed to charge stabilisation by the electronegative nitrogen atoms, which more than compensates for the decrease in aromaticity. In agreement with

migration of negative charge from the exocyclic oxygen atoms to the ring in aza derivatives, the exocyclic C-O bond lengths significantly shorten.

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Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/??????. These data include MDL files and InChiKeys of the most important molecules described in this article.

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- Relative stability of mesoionic rings increases with single bond strength (SS > RNNR > OO).
- Aromaticity of mesoionic rings decreases with ring aza substitution.
- Solvation stabilises type B mesoionic rings.