Valence tautomerism and recyclisation of type B mesoionic tetrazoles: a computational study

Wojciech Piotr Ozinski¹ · Christopher Antony Ramsden²

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Abstract
The energy profiles for ring opening of representative type B mesoionic 2,3-diphenyl-1,2,3,4-tetrazolium-5-olates, -thiolates, -aminides and –methylides and for alternative recyclisation pathways are investigated using ab initio MP2 calculations. The energetics of initial ring opening are found to be comparable for all systems, but the tetrazolium-5-olates are anomalous in that no alternative reaction pathway is accessible. The influence of solvent is explored using the polarised continuum model (PCM) method to simulate aqueous solvation. The only significant solvent effect is found to be solvation of the mesoionic precursors. This solvent effect correlates with dipole moment and disfavours initial valence tautomerism both kinetically and thermodynamically.

Keywords Mesoionic · MP2 Calculations · Valence tautomerism · Tetrazoles · Solvation · Recyclisation

Introduction

To gain a better understanding of the reaction pathways available to type B mesoionic tetrazoles, we have undertaken an MP2 ab initio study of the energy barriers to ring opening and recyclisation. We have previously studied the relative energies of ten type B mesoionic rings ¹ and their valence tautomers ². The stability of the ring increases with increasing strength of the single bond W-W (S–S > RN-NR > O–O) and with aza substitution (X = N) [¹].

The earliest report of an example of this class of heterocycle was the preparation of dehydrodithizone ³a by Fischer and Bestorn (1882) [²]. A preparation of the exocyclic oxygen analogue ³b was first reported by Bamberger (1898) [³, ⁴]. Other 1,2-diphenyl analogues are known. The exocyclic imine derivative ³c was described by Bamberger et al. [⁵] in 1926 but, as with derivatives ³a,b, only later was the mesoionic structure recognised [⁶]. The carbon analogue ³d was described by Neugebauer and Fischer (1980) but formulated as the tautomer ⁴d [⁷]. Based on spectral data (λmax 425) and the relative stability of closely related mesoionic tetrazoles, the open-chain structure ⁴d is only a transient intermediate in the formation of the mesoionic derivative ³d. Araki et al. in an NMR study have shown that the nitrile analogue ³e (λmax 468) is strongly favoured over the acyclic tautomer ⁴e [⁸].

In structures ³ and ⁴:
a, Y = S; b, Y = O; c, Y = N,NO; d, Y = CH,NO;
e, Y = C(CN)₂
Much of the chemistry of the mesoionic tetrazole derivatives 3a, c, d can be rationalised in terms of initial ring opening to the corresponding tautomers 4a, c, d. Dehydrothizone 3a is thermally transformed to the benzothiadiazin isomer 7a [9], which is almost certainly formed by recyclisation of a rotamer 5a to the intermediate 6a followed by proton transfer (Scheme 1). In a separate series of studies, Boyd et al. have provided evidence that the tautomer 5a can be trapped by 1,4-cycloaddition across the diazothione fragment [10–12].

In a re-examination of the work of Bamberger et al. [5], the derivative 3c has been shown to thermally rearrange to the N-oxide 9a, which is rationalised by recyclisation of the transient tautomer 8a (Scheme 2) [13, 14]. A similar mechanism accounts for the triazole 10 accompanying formation of the tetrazole 3d [7]. The mode of deoxygenation of the N-oxide precursor 9b is not clear.

Although the tetrazolium-4-olate 3b has been known for over 120 years, surprisingly, its chemistry is limited to salt formation [15, 16]. In contrast to its close analogue 3a, there is no experimental evidence of valence tautomerism (3 ⇌ 4). We now report a study of the energy barriers associated with reaction pathways available to the mesoionic tetrazole derivatives 3a–d.

### Results and discussion

Figure 1 shows the generalised energy profile for the ring opening of type B mesoionic rings 3 and recyclisation to the bicyclic products 7. Energy values (Hartrees) and energy differences (kcal mol⁻¹) for the derivatives 3–7 (Y = S, O, N.NO, CH.NO) and transition states T1 and T2 are given in Table 1.

### Gas phase MP2 calculations

The calculated activation energies ΔG₃T1 for ring opening via the transition state T1 (Table 1, Entries 1–4) are all in the range 26–31 kcal mol⁻¹. Since there is strong experimental evidence that the derivatives 3a, c, d do undergo thermal valence tautomerism in solution (3 ⇌ 4), it is unlikely that the oxygen analogue 3b will not undergo ring opening under similar conditions. As previously reported [1], the energy differences between the valence tautomers 3a, b, c and 4a, b, c (ΔG₃4) are in the range 16–18 kcal mol⁻¹. Interestingly, the ΔG₃4 value for the exocyclic carbon analogue 3d (10.29 kcal mol⁻¹) is much less. We attribute this to the lower electronegativity of carbon providing less stabilisation of the exocyclic negative charge in the mesoionic structure 3d. As might be expected, this also lowers the calculated activation energy ΔG₃T1 (26.18 kcal mol⁻¹).
To undergo an electrocyclic ring closure to give the intermediates 6, the valence tautomers 4 must equilibrate with a higher energy rotamer 5. The energy differences $\Delta G_{D1}$ are in the range 3.5–7.3 kcal mol$^{-1}$. A particularly significant difference between the sulphur and oxygen derivatives is the activation energy for electrocyclic ring closure ($\Delta G_{T2}$).

The sulphur tautomer 5a, known to lead to the isolated product 7a, has an activation energy $\Delta G_{T2}$ of 20.74 kcal mol$^{-1}$ (Table 1). In contrast, the oxygen analogue 5b has a significantly higher $\Delta G_{T2}$ value of 31.99 kcal mol$^{-1}$. Like the transition state, the oxygen intermediate 6b is also correspondingly higher in energy relative to the precursor 5b than the corresponding sulphur intermediate 6a. This is reflected in the reverse activation energies $\Delta G_{T2}$ (Table 1). These differences in the thermodynamics of the ring closures 5a, b to 6a, b have the consequence that the oxygen intermediate 6b is 43.47 kcal mol$^{-1}$ ($\Delta G_{36}$) higher in energy than the starting material 3b whereas the sulphur intermediate 6a is only 26.35 kcal mol$^{-1}$ ($\Delta G_{36}$) higher in energy. Since the energy of prototropic transfer (6 $\rightarrow$ 7) is almost the same for both species ($\Delta G_{67}$; 6a 27.35 and 6b 26.62 kcal mol$^{-1}$), it follows that the overall reaction of the sulphur derivative (3a $\rightarrow$ 7a) is calculated to be weakly exothermic ($\Delta G_{R1}$ $-1.00$ kcal mol$^{-1}$) whereas the corresponding reaction for oxygen (3b $\rightarrow$ 7b) is calculated to be considerably endothermic. Formation of the product 7b is therefore calculated to be highly unfavourable. This difference arises entirely from differences in the energies of the transition states $T_2$ and the resulting intermediates 6. For cyclisation of the oxygen analogue 5b, the activation energy for formation of the transition state ($\Delta G_{ST2}$) is much higher ($\approx$ 11 kcal mol$^{-1}$ more than for 5a), and the

| Entry | Y     | $G$ (Hartrees) | $\Delta G$ (kcal mol$^{-1}$) |
|-------|-------|----------------|-----------------------------|
|       |       | $G_{T1}$ $G_{T2}$ $G_{D1}$ $G_{D2}$ $G_{R1}$ $G_{R2}$ | |
| 1     | a. Y=S | -1115.825607 -1115.779662 -1115.796925 -1115.789162 | 28.83 4.87 18.00 26.35 |
| 2     | b. Y=O | -793.227336 -793.178146 -793.200781 -793.189235 | 30.87 7.25 16.66 43.47 |
| 3     | c. Y=N.NO | -902.358936 -902.309764 -902.330419 -902.324790 | 30.86 3.53 17.89 25.46 |
| 4     | d. Y=CH.NO | -886.313231 -886.271512 -886.296828 -886.291241 | 26.18 3.51 10.29 18.79 |
| 5     | a. Y=S | -1115.789162 -1115.756116 -1115.783613 -1115.827202 | 20.74 17.25 27.35 $-1.00$ |
| 6     | b. Y=O | -793.189235 -793.138252 -793.158064 -793.208810 | 31.99 12.26 26.82 16.65 |
| 7     | c. Y=N.NO | -902.324790 -902.283529 -902.318370 -902.373378 | 25.89 21.86 34.52 $-9.06$ |
| 8     | d. Y=CH.NO | -886.291241 -886.235227 -886.283283 -886.342460 | 35.15 30.16 37.13 $-18.34$ |
resulting intermediate 6b, relative to 5b, is also correspondingly higher in energy (≈16 kcal mol⁻¹ more than for 6a). This detracts from the overall energy of reaction (ΔG₁).

The cyclisations of the nitrogen and carbon species 5c, d merit comment although these derivatives have an alternative, more favourable, mode of cyclisation (Scheme 2). The cyclisation of the imine 5c is a little less favourable than for the sulphur species 5a. The activation energy is higher (ΔGST2 25.89 kcal mol⁻¹) but overall, the transformation 3c → 7c is exothermic (ΔG₉₁ -9.06 kcal mol⁻¹). For the carbon analogue 5d, the activation energy is highest (ΔGST2 35.15 kcal mol⁻¹), but much of this is regained on formation of 6d, and the tautomerism 6d → 7d is particularly favourable. Overall, the transformation 3d → 7d is calculated to be highly exothermic (ΔG₁ -18.34 kcal mol⁻¹); a contribution to this overall energy gain is the lower stabilisation (≈7 kcal mol⁻¹) of the polar precursor 3d by carbon, as discussed above.

Figure 2 shows the generalised energy profile for the alternative ring-opening/ring-closure reactions of the mesoionic derivatives 3c (Z = N) and 3d (Z = CH). The initial valence tautomerism (3 = 4) is identical to that in Fig. 1. The rotamers 8 then recyclise, employing the nitroso functions, to give the N-oxide products 9 via transition states T3. In both cases, the calculated activation energies (ΔGST3) are low (12–13 kcal mol⁻¹), and the overall reactions (ΔGR2) are exothermic (-13.66 and -22.83 kcal mol⁻¹ respectively) (Table 2). As noted previously, the reaction of the carbon analogue 3d is more exothermic, and this is attributable to the lower stabilisation of the mesoionic precursor 3d by the exocyclic carbon atom.

**Aqueous phase MP2-PCM calculations**

The energies and energy differences shown in Tables 1 and 2 relate to the gas phase. It is of interest to investigate the

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**Table 2** MP2 calculated energy values (G) and energy differences (ΔG) for the structures shown in Fig. 2

| Entry | Z  | G (Hartrees) | ΔG (kcal mol⁻¹) |
|-------|----|-------------|----------------|
|       |    | 8           | T3            | 9             | ΔG₁  | ΔGST2 | ΔGST3 | ΔG₉₁ | ΔGR2 |
| 1     | N  | -902.324790 | -902.304881   | -902.380707   | 3.54 | 12.49 | 47.53 | -13.66 |
| 2     | CH | -886.291241 | -886.270514   | -886.349611   | 3.51 | 13.01 | 49.63 | -22.83 |
influence of a polar solvent on the energy profiles. Taking water as an example, we have calculated the water-solvated free energies using the PCM (polarised continuum model) method to simulate aqueous solvation. The results for the reaction sequence $3 \rightarrow 7$ are shown in Table 3. A significant conclusion from these results is that solvent has little influence on the second phase of the reaction sequence $4 \rightarrow 5 \rightarrow T2 \rightarrow 6 \rightarrow 7$ (Fig. 1). For the parameters $\Delta G_p$, $\Delta G_{5T2}$ and $\Delta G_{67}$, the lowering of energy differences by solvent is small and in the range 0.3–2.0 kcal mol$^{-1}$. The only exception is $\Delta G_{5T2}$ for $Y=\text{CH-CN}$ (Entry 8) for which the energy difference is raised by solvent (−1.92 kcal mol$^{-1}$). Interestingly, the energy values for the reverse activation energies $\Delta G_{6T2}$ are increased in the range 0.6–1.0 kcal mol$^{-1}$ with the exception, again, of $Y=\text{CH-CN}$ which increases by 4.8 kcal mol$^{-1}$. Clearly, there is something a little different about the exocyclic CH-CN group, but overall, these small energy changes are of low significance and do not merit further discussion.

Solvent has a much greater effect on the first phase of the reaction sequence, i.e. $3 \rightarrow T1 \rightarrow 4$ (Fig. 1). We have previously reported that for isomers $3$ and $4$ ($Y=O,S$) aqueous solvation favours the cyclic mesoionic form by 10–15 kcal mol$^{-1}$ [1]. For the conjugated exocyclic groups ($Y=N.NO, CH.NO$), this solvation effect is greater. Table 4 shows the changes in calculated energy differences ($\Delta G$) upon solvation together with the calculated gas phase dipole moments ($\mu$). In Table 4, the effect of solvation on the energy difference $\Delta G_{34}$ is shown as $\Delta \Delta G_{34}$. The magnitude of the solvation effect ($\Delta \Delta G_{34}$) does correlate with the magnitude of the dipole moment although the particularly low solvent effect on the oxygen analogue (Entry 2) is surprising. A similar variation is seen for the solvent effect ($\Delta \Delta G_{3T1}$) on the activation energy $\Delta G_{3T1}$. Although of no particular significance, it is interesting to compare $\Delta \Delta G_{34}$ and $\Delta \Delta G_{66}$. The variations of these solvent effects are very similar and, since solvation has little effect on the intermediates $6$ (Tables 1 and 3), this effect can also be attributed to stabilisation of the dipolar precursors $3$.

The effect of solvation on the overall reaction energy $\Delta G_{R1}$ (Fig. 1) is of some interest. In all cases, the effect of the aqueous environment ($\Delta \Delta G_{R1}$) (Table 4) adversely affects the reaction energy, but this can all be attributed to stabilisation of the mesoionic precursors $3$. Again the smallest solvent effect is on the oxygen analogue (Entry 2), but this is not advantageous since the cyclisation $5 \rightarrow 6$ is particularly unfavourable compared to those of the $S, N.NO$ and CH.NO analogues.

Similar solvation effects are seen for the transformations $8 \rightarrow 9$ (Fig. 2). MP2-PCM energy values for aqueous solvation are shown in Table 5. Comparison with Table 2 shows that aqueous solvation effects are small (<3 kcal mol$^{-1}$) for the energies $\Delta G_{D2}$, $\Delta G_{S3T}$ and $\Delta G_{pT3}$. As for the formation of the products $7$, there is a significant aqueous solvent effect on the overall energy of reaction $\Delta G_{R2}$, but this can again be almost entirely attributed to solvent stabilisation of the mesoionic precursors $3c,d$. The solvent effects ($\Delta \Delta G_{R2}$) are 15.85 ($Z=N$) and 16.84 ($Z=CH$) kcal mol$^{-1}$, which are

### Table 3
Solvent MP2-PCM calculated energy values (G) and energy differences ($\Delta G$) for the structures shown in Fig. 1.

| Entry | Y  | G (Hartrees) | $\Delta G$ (kcal mol$^{-1}$) |
|-------|----|--------------|-----------------------------|
|       |    | $3$ | $T1$ | $4$ | $5$ | $\Delta G_{ST1}$ | $\Delta G_{ST2}$ | $\Delta G_{S6}$ | $\Delta G_{R1}$ | $\Delta G_{R2}$ |
| 1     | a  | $Y=S$ | $-1115.856429$ | $-1115.791484$ | $-1115.805278$ | $-1115.798086$ | $40.75$ | $4.51$ | $32.10$ | $37.74$ |
| 2     | b  | $Y=O$  | $-793.242707$  | $-793.192380$  | $-793.208322$  | $-793.199913$  | $37.86$ | $5.28$ | $21.58$ | $44.66$ |
| 3     | c  | $Y=N.NO$ | $-902.396906$ | $-902.325922$ | $-902.339817$ | $-902.335071$ | $44.54$ | $2.98$ | $35.82$ | $40.51$ |
| 4     | d  | $Y=CH.NO$ | $-886.353005$ | $-886.287863$ | $-886.306872$ | $-886.302128$ | $40.88$ | $2.98$ | $28.95$ | $34.03$ |
| 5     | a  | $Y=S$  | $-1115.798086$ | $-1115.767854$ | $-1115.796287$ | $-1115.838391$ | $18.97$ | $17.84$ | $26.42$ | $11.32$ |
| 6     | b  | $Y=O$  | $-793.199913$  | $-793.150897$  | $-793.171543$  | $-793.211805$  | $30.76$ | $12.96$ | $25.26$ | $25.67$ |
| 7     | c  | $Y=N.NO$ | $-902.335071$ | $-902.295975$ | $-902.332344$ | $-902.386481$ | $24.53$ | $22.82$ | $33.97$ | $6.54$ |
| 8     | d  | $Y=CH.NO$ | $-886.302128$ | $-886.243052$ | $-886.298779$ | $-886.356081$ | $37.07$ | $34.97$ | $35.96$ | $-1.93$ |

### Table 4
Calculated dipole moments and solvent effects

| Entry | Y  | Dipole Moment $\mu$ (D) | $\Delta G$ (kcal mol$^{-1}$) |
|-------|----|--------------------------|-----------------------------|
|       |    | $\Delta G_{34}$ | $\Delta G_{3T1}$ | $\Delta G_{S6}$ | $\Delta G_{R1}$ | $\Delta G_{R2}$ |
| 1     | a  | $Y=S$ | $14.8$ | $14.10$ | $11.92$ | $11.39$ | $12.32$ | – |
| 2     | b  | $Y=O$  | $12.5$ | $4.92$ | $6.99$ | $1.19$ | $9.02$ | – |
| 3     | c  | $Y=N.NO$ | $17.6$ | $17.93$ | $13.68$ | $15.05$ | $15.60$ | $15.85$ |
| 4     | d  | $Y=CH.NO$ | $18.1$ | $18.16$ | $14.70$ | $15.24$ | $16.41$ | $16.84$ |
consistent with the corresponding values for $\Delta\Delta G_{R1}$ 15.60 and 16.41 kcal mol$^{-1}$ (Table 4, Entries 3 and 4).

Conclusions

This MP2 study sheds some light on the paucity of known reactions of the mesoionic 2,3-disubstituted tetrazolium-5-olates 3b. The calculations indicate that the activation energies ($\Delta G_{5T2}$) for the electrocyclic ring formation 5 $\rightarrow$ 6 is much higher for the oxygen derivative 5b (31.99 kcal mol$^{-1}$) than for the known reaction of the sulphur analogue 5a (20.74 kcal mol$^{-1}$) (Table 1). It is possible that other thermal pathways may be accessible to the tautomer 5b at high temperature; there is no evidence that this has been investigated. The tautomer 5b may also be trappable by appropriate alkenes and alkynes.

The calculated effects of aqueous solvation on the reaction energetics shown in Figs. 1 and 2 are small with the exception of stabilisation of the mesoionic precursors 3. Only the energy differences directly related to the energy of the precursors 3 are significantly increased by solvation (i.e. $\Delta\Delta G_{34}$, $\Delta\Delta G_{3T1}$, $\Delta\Delta G_{36}$, $\Delta\Delta G_{R1}$ and $\Delta\Delta G_{R2}$) (Table 4), and these are consistently attributable to the solvent effect on the precursors 3. This is in accord with their polarity and the calculated dipole moments (Table 4). Clearly, for reactions of these species, the polarity of the solvent should be minimised.

Computational details

Calculations were performed using the Gaussian 16 program [17] at the ab initio Möller–Plesset MP2 level of theory [18]. The correlation consistent aug-cc-pVDZ (ACCD) basis set was used [19, 20]. All geometry optimizations were followed by frequency calculations to establish the nature of the stationary point and to calculate the ZPE and thermal corrections to Gibbs free energy. All obtained transition states have one imaginary frequency which connects the appropriate reactant and product. All minima on the potential energy surface have no imaginary frequencies. All calculations were performed for the gas phase and for the water environment modelled via polarizable continuum model (PCM) [21].

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Data Availability Additional data (geometric parameters and Gibbs free energies of optimized molecules) are available as Supplementary Information.

Declarations

Competing interests The authors declare no competing interests.

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Table 5 MP2-PCM calculated energy values (G) and energy differences ($\Delta G$) for the structures shown in Fig. 2

| Entry | Z   | G (Hartrees) | $\Delta G$ (kcal mol$^{-1}$) |
|-------|-----|-------------|-----------------------------|
|       |     | 8           | T3                          | 9 | G$_{D2}$ | G$_{S2}$ | G$_{D3}$ | G$_{S3}$ | G$_{R1}$ | G$_{R2}$ |
| 1     | Z= N| $-902.335071$ | $-902.313236$ | $-902.393414$ | 2.98 | 13.70 | 50.31 | 2.19 |
| 2     | Z= CH| $-886.302128$ | $-886.281437$ | $-886.362549$ | 2.98 | 12.98 | 50.90 | $-5.99$ |
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