

The influence of exocyclic lone pairs on the bonding and geometry of type A mesoionic rings

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Research Article

Keywords: Mesoionic, MP2 Calculations, pEDA, Anomeric effect, Hyperconjugation, Configuration, Pyran-2-imines

DOI: <https://doi.org/10.21203/rs.3.rs-340048/v1>

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Abstract

Based on structures determined by X-ray crystallography, *ab initio* MP2 calculations on type A mesoionic rings give geometries in good agreement with observed values. A study of four mesoionic ring systems, each with exocyclic oxygen, nitrogen or carbon groups, shows that the presence and configuration of exocyclic lone pairs significantly influences the geometry and configurational preference. Using a localised bond model, these effects are rationalised in terms of an anomeric interaction of lone pairs with the antibonding orbitals of adjacent σ bonds. In agreement with experiment, similar effects are calculated for pyran-2-imines.

Introduction

To investigate the influence of exocyclic lone pairs on the geometries, bonding and relative energies of type A mesoionic rings, we have studied four ring systems, each with exocyclic C=O, (*E*) and (*Z*) C=NPh and C=C(CN)₂ groups, using *ab initio* Moller-Plesset MP2 calculations. Early studies of the sydnones **1** (Scheme 1) did not support a polarised structure **1a** in which the ring is associated with an aromatic sextet. The C-O stretching frequencies (1768 cm⁻¹) and the exocyclic C-O bond lengths (1.20 and 1.215 Å) from X-ray studies are more consistent with the structure **1b** [1-3]. Another notable feature is the deformation of the bond angles C-C-O (135.7 and 135.5°) and O-C-O (119.2 and 121.2°). Thiessen and Hope in a study of 4,4'-dichloro-3,3'-ethylenebissydnone pointed out that the ring C-O bond (1.407 Å) is significantly longer than that in furan (1.362 Å)[2,3]. This led these authors to suggest that the resonance structure **1c** contributes to the unusual bond lengths and bond angles. They also implied a participation of the carbonyl oxygen lone pairs leading to a contribution from structures **1d** resulting in shortening of one C-O bond and lengthening of the other [2].

These unusual bond lengths and angles are recurring features of the geometry of type A mesoionic rings with an exocyclic oxygen and this is illustrated by comparing the crystal structures **2-6** (Figure 1)[1,4-7].

Similar bond angle distortions are seen in the crystal structure of the well-known analytical reagent nitron **7** (Figure 2), which is a type A mesoionic ring with an exocyclic imine function [8]. During a casual examination of the crystal structure of the azasydnone imine **8** [9], we noticed two significant differences. In structure **8** the exocyclic angles are almost equal and, in contrast to nitron **7**, the imine **8** has the opposite configuration. Steric effects probably force nitron to adopt the observed configuration. Since there are no obvious steric interactions in imine **8**, we presumed this adopts the most stable configuration and that this preference may be attributable to the orientation of the exocyclic nitrogen lone pair. Two other crystal structures of mesoionic imines have been reported [10,11]. In these 1,3-diazol-4-imines, of which structure **9** is typical, steric effects also control the configuration. We now report calculations that demonstrate the influence of the configuration of lone pairs on structural properties.

Results And Discussion

Table 1 shows calculated bond lengths and angles for the mesoionic 1,2,3-oxadiazole and 1,2,3,4-oxatriazole derivatives **10a-d** and **11a-d**. The configurations of the imines are defined as *cis* or *trans* by the relationship of the nitrogen lone pair to the ring C-O or C-NR bond; the use of *E* and *Z* nomenclature to define configuration varies with the ring system under consideration and is not a consistent terminology for comparing a series of rings.

Mesoionic rings with an exocyclic C=C(CN)₂ group are known [12-15]. We regard the enes **10d** and **11d** as structures that are not modified by the effects of exocyclic lone pairs and which, therefore, can be used as structural reference points. The effects of lone pairs are measured relative to these geometries. In Tables 1 and 2, φ_{15} and φ_{45} are the differences between the bond lengths in structures **10a-c** and **11a-c** and the corresponding bond lengths in **10d** and **11d**. Similarly, δ_{156} and δ_{456} measure the differences in the corresponding bond angles. The value Δ_{exo} is the difference between the exocyclic angles 1-5-6 and 4-5-6 for each structure. ΔG_{rel} are the relative free energies of the imine configurational isomers **10b,c** and **11b,c**.

The calculated gas phase geometries are in satisfactory agreement with the crystal structures **2**, **4** and **8** (Figure 1). Inspection of Table 1 reveals that lone pairs increase the length of the 1-5 bond (φ_{15}) but the effect of a *trans* lone pair (**10c** and **11c**) is greater and the effect of two lone pairs (**10a** and **11a**) is greatest. A smaller and opposite effect is seen for the 4-5 bond (φ_{45}); here the larger effect is for the *cis* lone pair and the effects are not additive. The bond angles are also influenced by the configuration of the lone pair. *Trans* lone pairs increase angle 1-5-6 (δ_{156}) and decrease angle 4-5-6 (δ_{456}); *cis* lone pairs have the opposite effect. Inspection of the values of Δ_{exo} indicates that *trans*-imines have the smallest calculated difference between the exocyclic angles and *cis*-imines have the largest difference. This observation is consistent with the experimentally determined structure **7**. It is also significant to note that the *trans* isomers **10c** and **11c** are calculated to be the most stable (ΔG_{rel}) in accord with structure **8**.

In a parallel study we have calculated the properties of the 1,3-diazoles **12** and the 1,3,4-triazoles **13**. Relevant structural properties are shown in Table 2. There is good agreement with the observed geometries of aryl analogues of **12a** [16], **12b** [10,11] and **13b** [8]. Comparison with the data in Table 1 reveals similar trends, with notable differences that can be attributed to differences in C-O and C-NMe bonds. Changes in the ring bonds (φ_{15} and φ_{45}) show the same trends but the effects are smaller for φ_{15} . Trends in bond angle change with exocyclic group (δ_{156} and δ_{456}) are comparable in the two series as are the values of Δ_{exo} . However, it is notable that for the imines **12b,c** and **13b,c** the *cis* isomers are of lower energy (ΔG_{rel}). This is in agreement with the crystal structures of rings **7** and **9** (Figure 2), and can be attributed to steric interactions in the *trans* isomers. In the *trans* isomers **12c** and **13c** the NPh rings are twisted away from planarity (30-40°) indicating energetically unfavourable interactions. Although the *cis* isomer **13b** is fully planar, the Ph group is also twisted in the *trans* isomer **13c** indicating steric interaction with C⁴H that is absent when replace by N⁴.

Using the localised bonding model, we rationalise the observed properties in terms of energetically favourable anomeric effects between the exocyclic lone pairs and the antibonding orbitals of the adjacent ring bonds. In the *trans* configuration **14** the lone pair overlaps with the antibonding orbital of the C-X bond ($n \rightarrow \sigma_{\text{CX}}^*$) (Figure 3). This stabilising interaction introduces an antibonding element into the C-X bond resulting in bond lengthening (φ_{15} positive) while reinforcing the exocyclic C=N bond. The overlap shown in structure **14** is probably increased by increasing the angle 1-5-6 (δ_{156} positive). In accord with general bond properties, the size of the antibonding lobe on the C⁵ carbon will be related to the polarity of the bond and will increase as the electronegativity of X increases. This is consistent with the observation of a greater effect in the C=NPh *trans* structures **10c** and **11c** (C-O bond) than in **12c** and **13c** (C-NMe bond) (Tables 1 and 2).

A similar analysis (Figure 3, Structure **15**) accounts for the effect of a *cis* lone pair on bond lengths and angles. In this case the *cis* lone pair interacts with the antibonding orbital of the C-C or N-C ring 4-5 bond. Again, the greatest effects are on the more polar N-C bonds (**11b** and **13b**). In the cases where the exocyclic atom is oxygen, both lone pairs influence the geometry. For the 1-5 bonds there is an additive effect but for the 4-5 bonds the combined effect is not significant. For the angles 1-5-6 and 4-5-6 there is a compromise between the effects of *cis* and *trans* lone pairs and Δ_{exo} has an intermediate value.

The anomeric effects described here are analogous to other hyperconjugative effects between the antibonding orbitals of polar bonds and adjacent lone pairs, which often account for conformational preferences [17]. Anomeric effects are sometimes attributed to dipolar or steric interactions. In the case of type A mesoionic structures these effects seem unlikely; the derivatives **11**, which have similar dipolar and steric characteristics regardless of configuration, have a similar profile to the other derivatives **10**, **12** and **13**. Within the localized bond model, other orbital interactions obviously influence relative energy and geometry. However, we believe that those shown in Figure 3 dominate. It is also important to recognise that, in addition to lone pairs, other factors influence ring geometries. These include the nature of ring heteroatoms as can be seen from the variation of Δ_{exo} for the dicyano derivatives (**10d** – **12d**, Tables 1 and 2).

We regard the dicyano derivatives as a realistic choice of reference structure. Analogues of this type are known [12-15,18-20], and the exocyclic group C=C(CN)₂ is a good lone pair-free electronic analogue of C=O and C=NAr. Unsubstituted derivatives C=CH₂ are of some interest for two reasons: (i) mesoionic examples of this type were prepared and fully characterised (with X-ray structures) in 2020 [21]; (ii) the CH bonds may show some hyperconjugative electron donation, in a manner analogous to lone pairs.

Table 3 compares calculated properties of C=C(CN)₂, *cis* and *trans* C=CHCN and C=CH₂ mesoionic 1,3-diazoles **16**. The results reveal some evidence of C-H hyperconjugation, especially by the *trans* CH bond in structure **16c**. Although the effects of the CH bonds in structures **16** are less than those of lone pairs, the trends in bond length and bond angle change are similar, and this suggests an analogous but smaller

anomeric effect. The isomer **16c** is less stable (ΔG_{rel}) than **16b**, and this is attributable to a small steric interaction between Me and CN.

The structure of the CH₂ derivative **16a** is of particular interest since, unlike the other mesoionic rings which are planar, the five-membered ring in structure **16a** shows distortion from planarity in both the calculated and X-ray structures (torsion angle 1-5-4-3: calc. 4.4°; obsd 4.2°). This can be attributed to an increased π electron population introducing anti-aromatic character. The index pEDA (pi Electron Donor-Acceptor) is the sum of the populations of the ring p_z atomic orbitals minus the aromatic sextet value of six [22]. The pEDA values for the ene structures **16a-d** are shown in Table 3. The π -electron ring population of **16a** is demonstrably higher than the cyano derivatives **16b-d** and also the oxygen and nitrogen derivatives **12a-c** (pEDA: **12a** 0.230; **12b** 0.262; **12c** 0.192). Overall the dicyano derivatives have comparable properties to oxygen and nitrogen analogues and are realistic hyperconjugation-free references structures for studying the influence of lone pairs.

To explore whether similar anomeric effects are found in other heterocyclic rings with exocyclic substituents, we have calculated properties of the pyrone derivatives **17a-d**. *N*,4,6-Triphenypyran-2-imines are known [23,24], and Uncuța and coworkers, in a detailed NMR study, have shown that in equilibrium mixtures, e.g., **17b,c**, the *trans* (*Z*) configuration prevails [25].

Examination of Table 4 reveals that the structural changes in the series **17a-d** are similar to the trends in Tables 1 and 2. It is noteworthy that the angle difference Δ_{exo} is smallest for the *trans* isomer **17c** (+1.8°) and largest for the *cis* isomer **17b** (+15.0°); this closely parallels the analogous structures **10** and **11** (Table 1). In agreement with experimental data [25], the *trans* isomer **17c** is calculated to be the more stable (ΔG_{rel} -0.23 kcal mol⁻¹) (Table 3).

Conclusions

MP2 calculated geometries of type A mesoionic rings are in good agreement with reported crystal structures. *Cis* and *trans* lone pairs on the exocyclic heteroatoms have different effects on bond lengths, bond angles and total energies. For exocyclic imino groups (C=NAr), in the absence of steric effects, the *trans* configuration is favoured energetically. Within the localised bond model, these effects are rationalised in terms of anomeric interactions of lone pairs with the antibonding orbitals of adjacent σ bonds, resulting in bond lengthening. These results provide some insight into the structures of type A mesoionic rings which generally have a short exocyclic bond and a particularly long ring C-X heterobond (e.g., **1b**), rather than a ring associated with an aromatic sextet (e.g., **1a**). In agreement with experiment, similar structural effects are seen in pyrone derivatives.

Computational Details

Calculations were performed using the Gaussian 16 program [26] at the *ab initio* Moller-Plesset MP2 level of theory [27]. The correlation consistent aug-cc-pVDZ (ACCD) basis set was used [28,29]. Geometric

parameters of all molecule were fully optimized at the MP2/aug-cc-pVDZ level of theory. 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 minima on the Potential Energy Surface have no imaginary frequencies.

Declarations

Acknowledgements

Computational Grant G36-9 from the Interdisciplinary Centre for Mathematical and Computational Modelling at Warsaw University (ICM UW) is gratefully acknowledged

Funding

Not applicable

Conflicts of interest/Competing interests

The authors declare that they have no conflict of interest

Availability of data and material

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

Code availability

Not applicable

Authors' contributions

Not applicable

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Tables And Scheme

Tables 1-3 and Scheme 1 are available in the Supplementary Files.

Figures

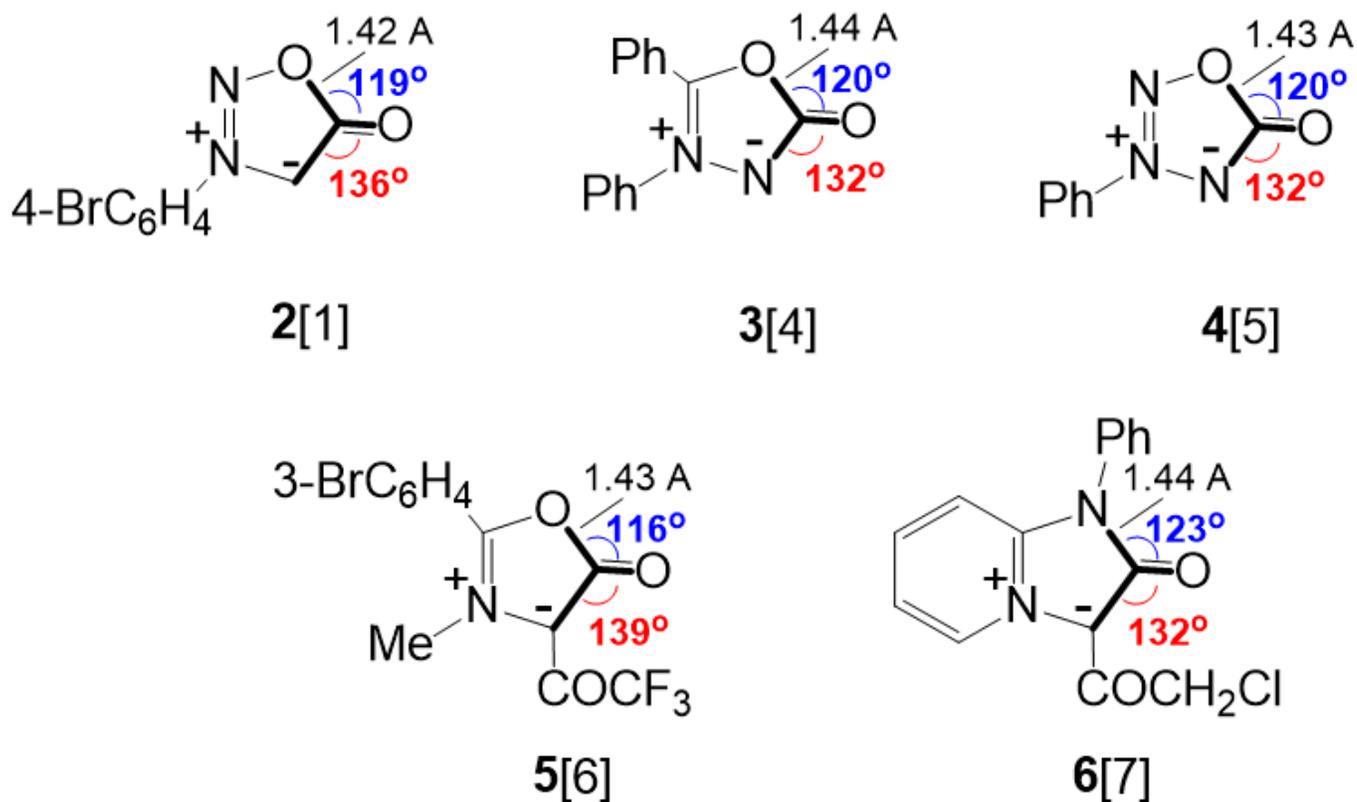


Figure 1

X-ray determined geometries of type A mesoionic rings with an exocyclic C=O group.

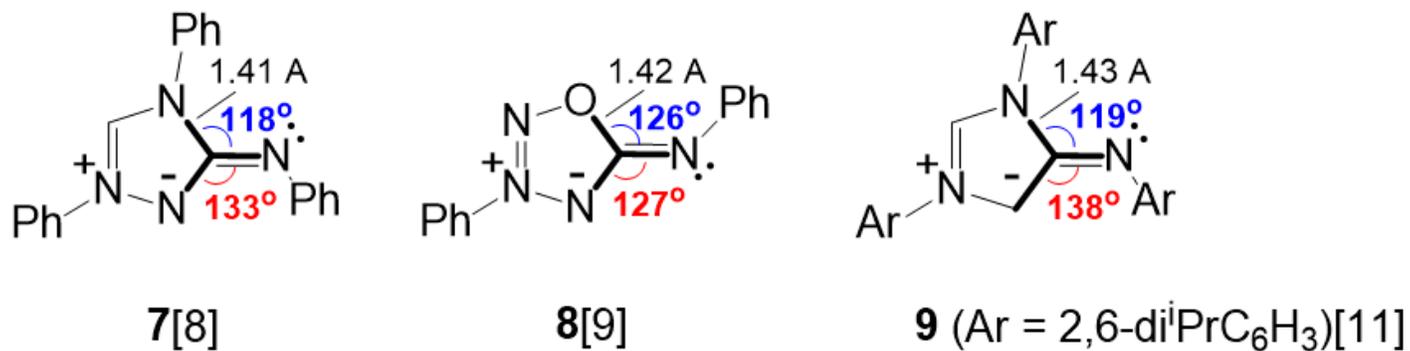
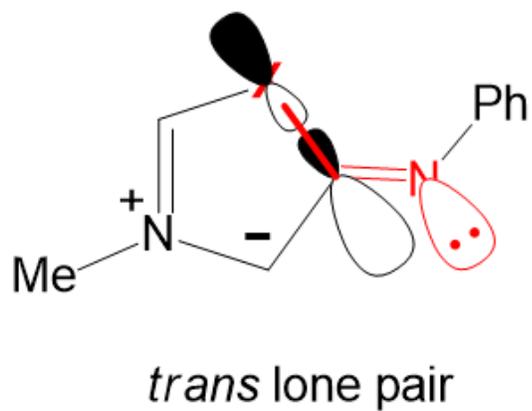
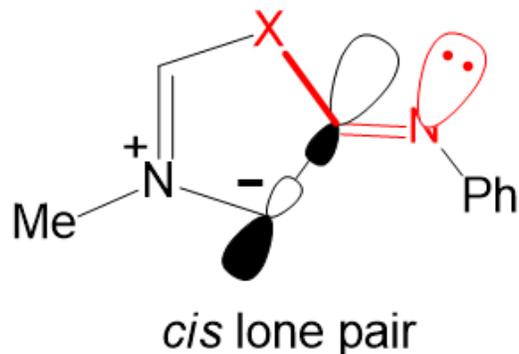


Figure 2

X-ray determined geometries of type A mesoionic rings with an exocyclic C=NAr group.



14



15

Figure 3

Anomeric Interactions Between *trans* and *cis* Lone Pairs on Adjacent Ring Bonds.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Table1.png](#)
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