



## Tautomerism in polyguanide

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### ABSTRACT

Tautomerism in polyguanide is theoretically discussed. For biguanide, triguanide (melamine), and linear polyguanides, stability of the most stable tautomer is investigated by semi-empirical and DFT calculations. Amino tautomers are more stable than the corresponding imino tautomers, and the energy gaps are ca. 6–7 kcal/mol per guanide unit. In polyguanides, amino tautomers with *cis*-type  $\text{—N=C—N=C—}$  chains are preferred, and flat bands appear near the non-bonding level. Based on the *cis*-amino tautomers, applications to metal-complexing agents and magnetic materials are proposed.

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### 1. Introduction

Cyanamide derivatives often exhibit tautomerism due to proton transfer. The tautomerism resembles that of vinyl alcohol, in which the keto and enol structures coexist. In cyanamide derivatives such as biguanide, amidinourea (guanylurea), biuret and so on, discussions on the most stable structures have been somewhat confused by many speculations. Fig. 1 shows possible tautomerism of biguanide and the protonation process. For the neutral biguanide, early workers gave the conventional structure with two-imino groups, as shown in Fig. 1a [1]. Fabbrizzi et al. concluded from negative entropy of protonation that the most stable structure of the biguanide is the symmetric one Fig. 1a [2]. They speculated that the negative entropy of protonation suggests a 'flexible' structure with single bond moieties in the neutral state and a 'rigid' structure with fully conjugated double bonds in the mono-protonated form.

On the other hand, biguanide shows ultra violet (UV) absorption at 230 nm. Under strongly acidic condition, however, the peaks of spectra shift toward vacuum ultra violet region. Hirt and Schmitt concluded from the UV spectra that the structure in Fig. 1b was the most stable isomer of neutral biguanide, and the disappearance of UV spectra under acidic condition was attributed to the di-protonated structure [3]. This is reasonable in that the UV spectra are attributed to  $\pi$  conjugation of the  $\text{—N=C—N=C—N—}$  chain in Fig. 1b, and the blue shift of the spectra are due to the separated two pairs of amino groups in the dicationic state, as indicated in the bottom of Fig. 1 [3,4]. Indeed, X-ray analysis of solid-state biguanide supported the asymmetric structure Fig. 1b [5] and the

symmetric structure of the monocationic state as hydrochloride shown in the middle of Fig. 1 [6]. As for X-ray analyses on neutral, monocationic, and dicationic states, see also another literature [7]. Nowadays, however, many medicinal chemists still adopt the conventional structure with two-imino groups shown in Fig. 1a. In solution, this structure may exist to some extent because of the solvation or proton exchange. However, NMR spectra of a typical aryl derivative *o*-tolylbiguanide have only two distinguishable protons with integral ratio ca. 1:5 at  $\delta = 3\text{--}5$ , which suggest the asymmetric structure [8]. Therefore, at least at the room temperature, the symmetric structure is considered to be quite unstable relative to the asymmetric structure. Although biguanide derivatives have been widely used as sanitizing agent, oral hypoglycemic agent, basic catalysis and so on, it was not until an *ab initio* study was performed systematically in 2005 that the structural details on the tautomerism were theoretically established by Bharatam et al. [9]. They showed stability of the asymmetric structure in view of reliable quantum chemistry for the first time.

There are many tautomers in biguanide. Fig. 2 shows five of them: **1** is an imino tautomer with a  $C_{2v}$  geometry, which is familiar to us as the conventional structure. **2** is the atrop isomer of **1**. The electronic repulsion between lone pairs on the nitrogens is reduced, and additional stability due to the hydrogen bonding between the imino moieties is expected. **3** is an amino tautomer. The steric hindrance between the hydrogen atoms are considered to be quite large. **4** is another imino tautomer. This structure is deduced from **1** by rotation around the C—N single bond. **5** is another amino tautomer. The structure is deduced from **3** by rotation around the C—N single bond. As clarified later, **1**, **2**, and **3** are the simplest *trans*-type polyguanides, and **4** and **5** are the simplest *cis*-type polyguanides.

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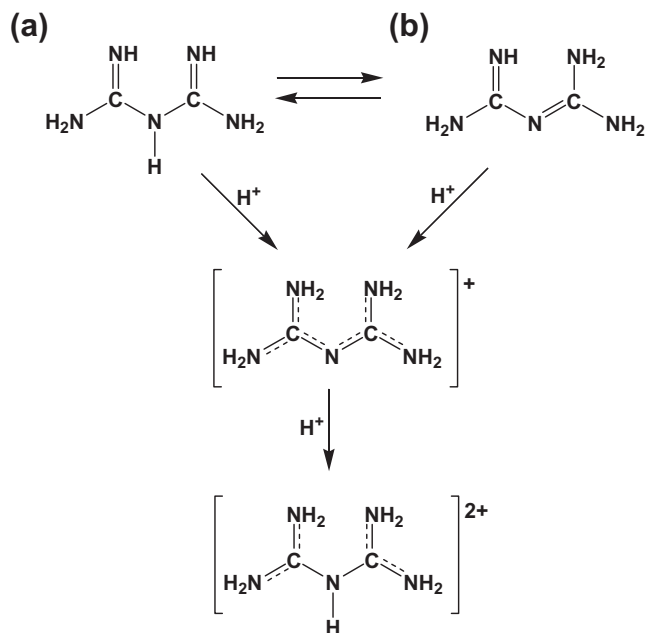


Fig. 1. Molecular structures of biguanide and its mono- and di-protonated forms.

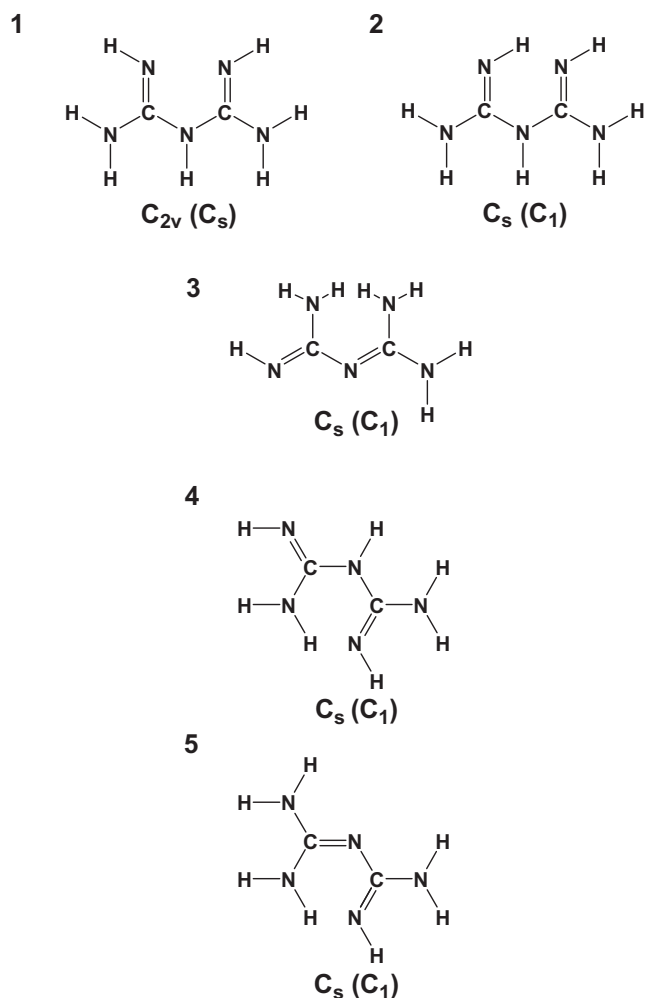


Fig. 2. Tautomers of biguanide. 1, 2, and 4 are imino rich, 3 and 5 are amino rich. The symmetry classifications are given for the planar (non-planar) geometries.

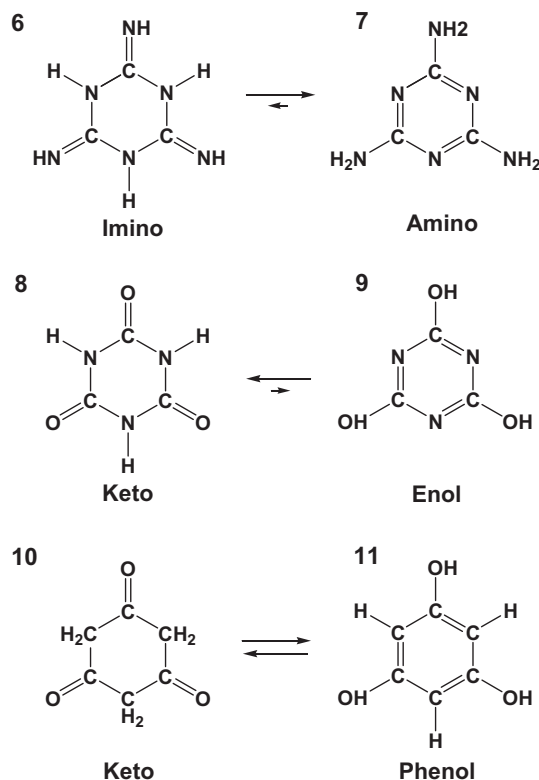


Fig. 3. Tautomerism of melamine (6 and 7), cyanuric acid (8 and 9), and phloroglucinol (10 and 11).

Melamine (6 and 7 in Fig. 3) is regarded as a trimer of guanide unit. This is a familiar compound as an ingredient for robust thermosetting resins. As is not so well known, imino–amino tautomerism is also possible in this compound. One is the conventional structure with three amino groups, and another is the corresponding imino tautomer. UV spectra suggest that the stable structure of melamine is the amino type [3]. However, quantum-chemical calculations on the tautomerism have not been done in detail. Theoretical analysis of this tautomerism should give an important perspective on chemistry of polyguanides. Tautomerism of melamine is interesting as a comparative study with that of cyanuric acid (8 and 9) and phloroglucinol (10 and 11), as shown in the middle and bottom of Fig. 3, respectively.

Moreover, much attention has been paid to polyguanides due to their possible superbasic property [10] or magnetic ordering in the cationic states [11]. In 2000, Maksić and Kovačević theoretically proposed superbases, of which structures contain four or seven guanide units [10]. In the original paper, tetraguanide and heptaguanide proposed by them are not linear molecules but branched dendrimers. Since the atomic sites are divided into starred and unstarred atoms that are not adjacent each other, there should be non-bonding orbitals in polyguanides, of which amplitudes are mainly localized at the nitrogen atoms. Thus, in polyguanides, non-bonding  $\pi$  orbitals and lone pairs should be nearly degenerate and coexist at the frontier level. In 2004, we proposed possible magnetic materials taking advantage of the non-bonding characters of linear polyguanides [11]. In these linear polyguanides, the tautomerism is also an open question. In view of synthetic technique, polymerization of polyguanides is also an interesting theme, because linear polyguanides have not been well analyzed except for triguanide. In linear polyguanides, pseudo non-bonding crystal orbitals should exist instead of non-bonding molecular orbitals. Polyguanide is regarded as an analogue of polyurea, which is also a mysterious polymer of which structure has not been established

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