

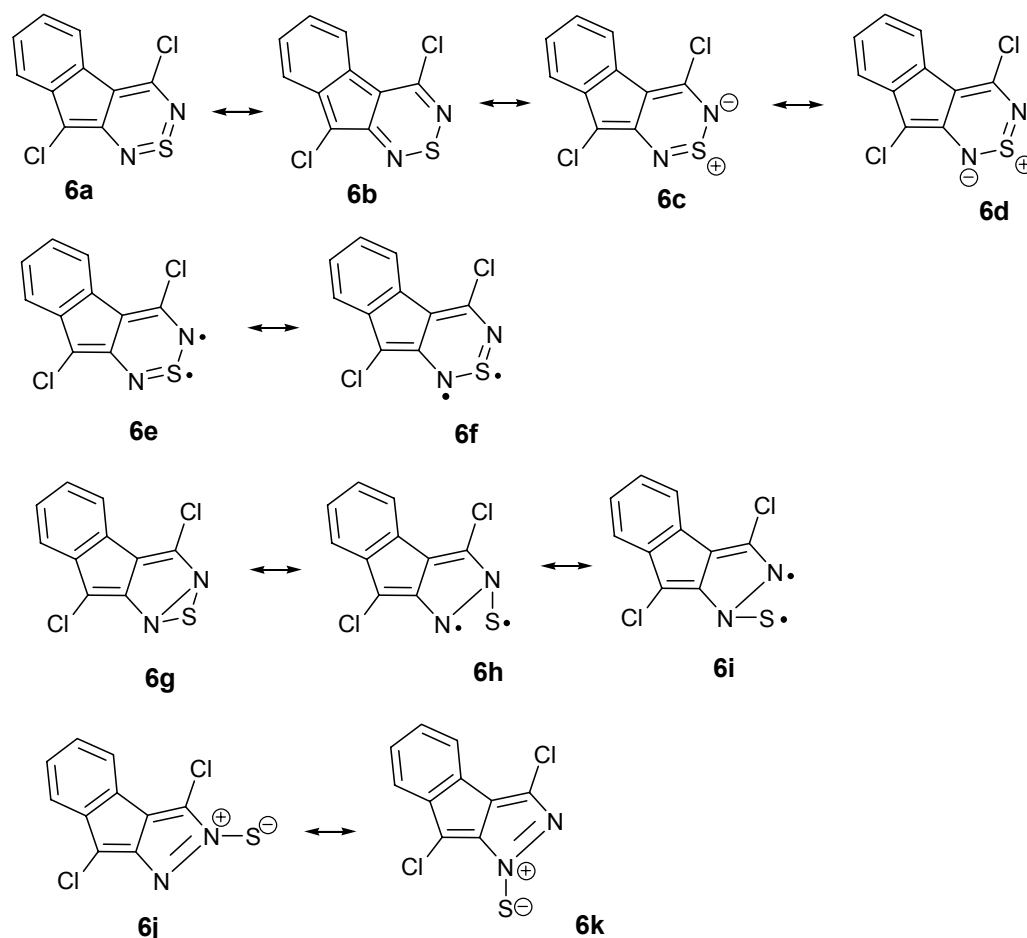
Cyclopentathiadiazines, new heterocyclic materials from cyclic enaminonitriles.

Sonia Macho,^a Daniel Miguel,^b Ana G. Neo,^a Teresa Rodríguez,^a and Tomás Torroba^{*a}

^a Departamento de Química, Facultad de Ciencias, Universidad de Burgos, 09001 Burgos, Spain. Fax: 34 947 258087; Tel: 34 947 258088; E-mail: ttorroba@ubu.es

^b Departamento de Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain; E-mail: dmsj@qi.uva.es

Some considerations about the structure of compound **6**.



The most surprising feature of compound **6** is the difficulty to assign a unique structure that defines correctly the bonding of **6**. Structure **6a** contains an oxidized sulfur having a valence state +4, structure **6b** has an unlike quinodimethane moiety, although sulfur exists as a reduced valence state +2. Charged forms **6c** and **6d** are more likely stable than **6a-b** because they keep an aromatic benzene fused ring and a less oxidized sulfur atom, although they have separate charges. In this case the sulfur atom is clearly the donor atom and the nitrogen atoms are alternatively the acceptor atoms. But non-charged structures are also possible. Structures **6e** and **6f** are bi-radical species having the same bonding as **6c** and **6d** but without separate charges. All structures **6a-f** are 14 π aromatic species, so all of them are possible. But some other structures are also possible. Structure **6g** has the lowest oxidation

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state for the sulfur atom, but has a three-membered heterocycle that is not very stable. Opened forms of **6g** are the bi-radical structures **6h** and **6i**, that are 13π aromatic species, and the less likely 12π antiaromatic charged structures **6j** and **6k**. What is the most plausible structure that explains all experimental features of compound **6** poses a challenging question to the theoreticians. *Ab-initio* calculations (Unrestricted Hartree-Fock, 6-31G*) of structure **6** give a structure that combines **6c-f** species, with a partial positive charge on the sulfur atom and partial negative charges on the nitrogen atoms, and a SOMO that is mainly localized on the sulfur atom. But this type of calculation is not conclusive although a diffuse radical system mainly localized between the sulfur and the nitrogen atoms can be expected to have little influence on the nuclear spins of the far hydrogen atoms and so on the NMR spectra.