Electrochemical proof of the single bond character of the N-N bonds in some 1,2,4-triazines

J Ludvik$^a$ & P Zuman$^b$

$^a$J. Heyrovsky Institute of Physical Chemistry, Academy of Science of the Czech Republic, Dolejskova 3, 182 23, Prague 8, Czech Republic

$^b$Department of Chemistry, Clarkson University, Potsdam, NY 13699-5810, USA

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Whereas in molecules containing grouping $X=C-C=Y$ ($X, Y = C, 0, N, S$) delocalization of electrons takes place, in compounds containing the grouping $C=N-N=C$ the central N-N bond has a single bond character and conjugation does not play a role. The single bond character of the N(1)-N(2) bond in 1,2,4-triazin-5-ones has been confirmed based on identity of reduction potential of the 1,6-azomethine bond in the parent compound and of the 1,6-C=N bond in the corresponding 2,3-dihydro derivative. Lack of delocalization has also been proved for acyclic azines. Comparison of half-wave or peak potentials is a simple and efficient way to prove or disprove the role of the delocalization of electrons over the studied molecule.

To prove a delocalization of electrons in crystalline organic molecules, it is possible to evaluate measurements of bond lengths and bond angles using X-ray crystallography. For organic compounds in solutions the delocalization can be experimentally investigated using IR, Raman and various NMR spectra.

In a simple and direct way, it is, however, possible to obtain information about the delocalization using electrochemical measurements. This is made possible by a comparison of the reduction potential of a compound bearing the grouping $X=C-C=Y$ with that of a compound which bears the grouping $X=C-CH_2$. In delocalized systems the reduction of the group $X=C$ in $X=C-C=Y$ occurs at significantly more positive potentials than the reduction of the same group $X=C$ in $X=C-CH_2$. The difference of the two potentials increases with increase in the extent of delocalization. Absence of delocalization in such systems is manifested by identity of these two potentials.

The delocalization in systems including groupings $X=C-C=Y$ (where $X$ and $Y$ are $C$, $O$, $S$, or NR) has been in the past confirmed using reduction potentials for numerous acyclic and cyclic organic compounds. It is the aim of this paper to draw attention to the fact that in cyclic and acyclic compounds, bearing the grouping $C=N-N=C$ with a central N-N bond, the delocalization is very limited or absent.

In solutions of some 1,2,4-triazin-5-ones (for example, 4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4)H-one and 4-amino-3-methylthio-6-tert-butyl-1,2,4-triazine-5(4)H-one) the reduction of the protonated form of the 1,6-azomethine bond occurs over the entire pH-range at potentials more than 0.5 V more positive (that is much easier) than that of the protonated 2,3-azomethine bond. More importantly for the present discussion, when the reduction potential of the 1,6-azomethine bond in the parent 1,2,4-triazin-5-one was compared with the reduction potential of the 1,6-azomethine bond in 2,3-dihydro-1,2,4-triazin-5-one, it was observed that the two potentials are identical (within ±0.002 V, from pH 1 to 10). This means that the reduction of the 1,6-azomethine bond in a 1,2,4-triazin-5-one occurs at the same potential irrespectively, whether in the 2,3-position is present a C=N or a CH-NH grouping. Identity of potentials of the grouping $>C=N-N=C<$ in the parent compound with those of the $>C=N-NH-CH<$ grouping in the dihydro derivative indicates absence of delocalization via the N-N bond.

Absence of delocalization is further supported by the effects of substituents on reduction potentials. The half-wave potentials of the reduction of the protonated form of the 1,6-azomethine bond are shifted by variations of substituents at C-6. Observed shifts fit the modified Taft equation, as corresponds to a LFER. On the other hand, a change in a substituent at C-3 does not affect the half-wave potentials of reductions of the 1,6-azomethine bond.

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In the triazine ring in these molecules, the effect of the substituent at C-3 is not transmitted through the ring, as it is observed for delocalized and aromatic systems.

Limited delocalization has been reported\(^\text{4}\) for 5-(p-chlorophenyl)-1,2,4-triazine where in solid state the length of the N(1)-N(2) bond (\(r=1.335\) Å) corresponds to about \(n=1.3\) using Pauling’s equation. This and MO calculations enabled authors to conclude that "the canonical structure of 1,2,4-triazine with a N(1)-N(2) single bond more closely represents the ground state of this ring system than that with N(1)-N(2) double bond."

The lack of conjugation in the presence of an N-N bond is not restricted to heterocyclic compounds studied. In the fifties it has been reported\(^\text{5}\) (but not discussed) that reduction potentials of benzalazine \((\text{C}_6\text{H}_5\text{CH}=\text{N}=\text{N}=\text{CH}_2\text{C}_6\text{H}_5)\) and benzyl benzaldehyde hydrazone \((\text{C}_6\text{H}_5\text{CH}=\text{N}-\text{NH}-\text{CH}_2\text{C}_6\text{H}_5)\) are practically identical, i.e., the presence of the second C=N bond does not affect the reduction of the first one. Hence the absence of delocalization in molecules containing a =N-N= grouping seems to be a more general phenomenon.

For acyclic azines this conclusion has recently been also arrived at in contributions dealing predominantly with conformation of molecules bearing an N-N bond. The attribution of the single bond character of the N-N bond in various substituted acetophenone azines was based on X-ray crystallography, IR, Raman and NMR spectra and MO calculations\(^\text{6-10}\).

Extension of conclusions about the prevention of delocalization in molecules containing an N-N bond to other types of heterocyclic (e.g., 1,2-diazines) and acyclic compounds bearing the groupings >C=N-N=C< and >C=N-N-N< is in progress as well as a theoretical approach using \textit{ab initio} quantum chemical calculations.

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**References**