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Lack of delocalization in compounds with the grouping C=N–N=C

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Abstract

Whereas for molecules containing the grouping X=C–C=Y (X, Y = C, O, N, S) delocalization of electrons is well established, it is concluded here that in both cyclic and acyclic compounds containing the grouping C=N–N=Z (Z = C, N) the delocalization is either minimal or absent. Electrochemically determined reduction potentials are a useful tool for estimating the extent of conjugation. © 2000 Elsevier Science Ltd. All rights reserved.

There is an abundance of evidence for the delocalization of electrons in systems containing the grouping X=C–C=Y (where X, Y = C, O, N, or S), but no general statement has been found dealing with the delocalization involving the grouping C=N–N=Z (where Z is C or N). Some scattered information, indicating limiting or lacking delocalization can be found in the literature. An example of such a system in a heterocyclic compound is 5-(*p*-chlorophenyl)-1,2,4-triazine (I) where, in the solid state, the length of the N(1)–N(2) bond (Table 1) corresponds to about $n = 1.3$ using Pauling's equation. This and MO calculations enabled authors[1] to conclude that "the canonical structure of 1,2,4-triazine with an N(1)–N(2) single bond represents the ground state of this ring system more closely than that with an N(1)–N(2) double bond." For metribuzin (II) the n value for N–N bond was[2] 1.23 and for 1,2,4-triazole (III) $n = 1.24$. The longer length of the central N–N bond is not restricted to heterocyclic compounds. For anisaldehyde[3] (IV) and salicyaldehyde[4] (V) azines n was found to be 1.0. Simultaneously, the C=N bonds are rather short, $r = 1.283$ Å for anisadehyde[3] and 1.274 Å for salicyladehyde[4] azine. In acetophenone azines[5–8] (VI) n was found to vary between 1.19 and 1.0 and the single bond character of the N–N bond was supported by IR, Raman, and NMR spectra and MO calculations.

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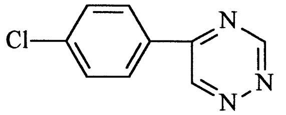
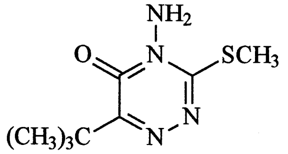
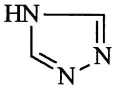
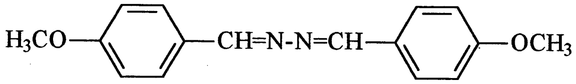
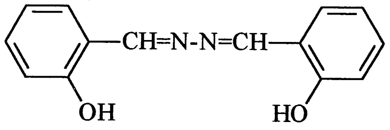
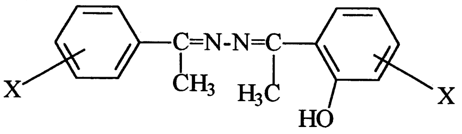
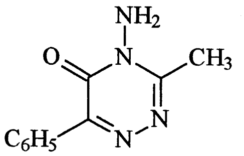
Table 1
Crystallographic data for the length of the N–N bond in some azines

		r of N-N Bond (Å)
I		1.335
II		1.359
II		1.354
IV		1.410
V		1.407
VI		1.375 to 1.409
VII		

To contribute more proof of the lack of delocalization in molecules containing the grouping C=N–N=C, electrochemical data are used in this contribution. Using such data, delocalization can be proved by comparing the reduction potential of a compound bearing the grouping X=N–N=Y with that of a compound which bears the grouping H_2C–NH–N=Y. The difference between the two potentials increases with increasing extent of delocalization. The absence of delocalization in such systems is manifested by the identity of these two potentials.

We proved the absence of delocalization by following the behavior of some 1,2,4-triazin-5-ones (e.g. metamitron[9] (VII) and metribuzin[10] (II)) where the potential of the reduction of the protonated form of the 1,6-azomethine bond in the parent 1,2,4-triazine-5-one is equal to (within ±0.002 V from pH 1 to 10) the reduction potential of the 1,6-azomethine bond in 2,3-dihydro-1,2,4-triazin-5-one. The reduction of the 1,6-azomethine bond in 1,2,4-triazin-5-one thus occurs at the same potential irrespective of whether a C=N or a CH–NH grouping is present at the 2,3-position. Comparing the potentials of the grouping $>$C=N–N=C$<$ in the parent compound with those of the $>$C=N–NH–CH$<$ grouping in the dihydroderivative indicates the absence of delocalization via the N–N bond.

The absence of delocalization is further supported by the effect of substituents on the reduction potentials.[11] 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,[12] corresponding to an 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. In the triazine ring in these molecules, the effect of the substituent at C-3 is thus not transmitted through the ring, as observed for delocalized and aromatic systems.

Electrochemical data also indicate the lack of delocalization in acyclic systems bearing a C=N–N=C grouping. In the 1950s it was reported[13] (but not discussed) that reduction potentials of benzalazine ($C_6H_5CH{=}N{-}N{=}CHC_6H_5$) and benzyl benzaldehyde hydrazone ($C_6H_5CH{=}N{-}NH{-}CH_2C_6H_5$) are practically identical, i.e. the presence of the second C=N bond does not affect the reduction of the first one.

Hence available data indicate that a limited or lack of delocalization in molecules containing the grouping C=N–N=C is a general phenomenon. Preliminary results, based on low values of reaction constants for substituent effects on reduction potentials of substituted triazenes, indicate also a limited delocalization in the grouping $>$C–N=N–N$<$.

Acknowledgements

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