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Bond orders and electron delocalization indices for S–N, S–C and S–S bonds in 1,2,3-dithiazole systems

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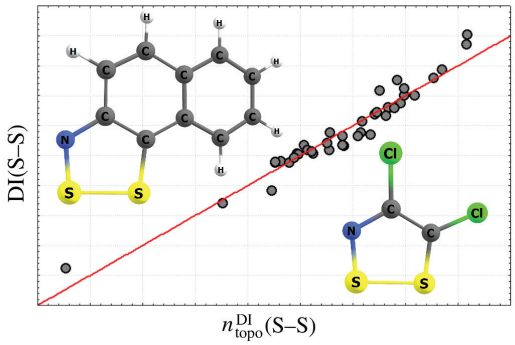
A parametric QTAIM-based (topological) model of bond orders and a modification of the Pauling bond order model are proposed for N,S-containing heterocycles, in particular, for 1,2,3-dithiazoles and 1,2,3-dithiazolium systems, which are prone to the formation of stable radicals and therefore are promising compounds in photovoltaics. These models have been parameterized for covalent S–N, S–C and S–S bonds using the electron delocalization indices. A modified Pauling's bond order model uses turning radii, that is, the distances within which the potential acting on an electron in a system still tends to return that electron to the atomic basin, and avoids the need to choose the hybridization state of bound atoms arbitrarily.



Keywords: bond orders, electron delocalization indices, turning radii, 1,2,3-dithiazoles, disulfide bond.

Five-membered N,S-heterocycles, in particular, 1,2,3-dithiazoles,[1–5] are one of the important classes of compounds promising to synthesize stable radicals.[6,7] In the crystalline state, they exhibit physical properties necessary for creating molecular magnets and conductors.[8–11] Biologically active compounds among the substituted 1,2,3-dithiazoles exhibit antitumor, antiviral, anti-inflammatory, antimicrobial and anti-tuberculosis activity.[12–14] In this regard, it is of interest to identify the features of the chemical bond and predict the reactivity and other properties of a 1,2,3-dithiazole system. An essential role in forming the unique electronic properties of 1,2,3-dithiazole systems belongs to the disulfide bond (S–S), which was recently studied in several works.[15–17] Due to the diverse possibilities of electron delocalization, 1,2,3-dithiazoles can exist as cations, radicals, radical cations or electrically neutral molecules. The bond orders in these molecules depend on substituents, conjugation and the presence of fused rings, which makes the behavior of covalent S–N, S–C and S–S bonds during redox processes unpredictable. Therefore, it is necessary to develop a bond order model that can reliably describe and predict bond orders for sulfur-containing molecular systems.

The classical approach to the estimation of covalent bond order was proposed by Pauling.[18] His equation describes the exponential dependence of the bond order *p*(A–B) on the difference between the bond length and the sum of covalent radii of A and B atoms. To choose the correct covalent radii, one needs to establish the atomic hybridization of the bonded atoms. Fortunately, the recently proposed concept of the 'turning' atomic radii[19–21] avoids this problem. Considering the potential acting on an electron in a molecule (PAEM),[22] we can determine the distance from the atomic nucleus to the point at which PAEM is equal to the first vertical ionization energy of the system. This distance was identified with the turning radius, the distance at which PAEM can still turn an electron, keeping it in a given atomic basin.[19–21] It is noteworthy that these radii do not depend on the conjugation of electrons in the system.

There are many schemes for estimating bond order indices.[23–27] Matta *et al.*[28,29] calibrated the equation proposed by Bader,[30] which expresses the exponential dependence of bond order on the electron density at bond critical points. The bond orders obtained from the electron delocalization indices were used. Further, an analysis of the matrix composed of the localization and delocalization indices was proposed[31] to assess the physicochemical properties and biological activity of compounds in the ground and excited states.

In this work, we focus on parametric models[32] based on the QTAIM characteristics.[33–35,†] Our sample includes 1,2,3-dithiazole derivatives and 1,2,3-dithiazolium cations, as well as dithiolethiones, thiazolethiones, thiadiazolethiones, dithiadiazoles and other derivatives of five-membered N,S-heterocycles (Table S1, see Online Supplementary Materials). The found characteristics of the electron density at the bond critical points, as well as the equilibrium interatomic distances and the electron delocalization indices DI(A–B) for the S–N,

† The equilibrium geometry of N,S-heterocycles was localized by the Kohn–Sham method using the PBE0 functional and the aug-cc-pVTZ basis set; the Firefly 8.0.1 software was used.[46] The quantum topological analysis of electron density and the calculation of electron delocalization indices were carried out using the AIMAll Professional program.[47] The search for fitting parameters in all multiple regressions was carried out using the Gauss–Newton method in the Statistica software;[48] as a loss function, we used least squares.

S–C and S–S bonds in the compounds under consideration, are given in Tables S2–S4.

There is a simple way to estimate the topological bond order n_{topo}(A–B) from the quantum-topological characteristics at the bond critical point. On the other hand, since the electron delocalization index is linearly correlated with the formal bond order, we used DI(A–B) as the response in the equation to estimate the topological bond order n^{DI}_{topo}(A–B). As factors in the equation, the model includes the electron density $\rho(r_b)$ and the eigenvalues $\lambda_1(r_b)$, $\lambda_2(r_b)$ and $\lambda_3(r_b)$ of the Hessian of electron density at this point.

Different fitting parameters are required for different types of covalent bonds. A number of such parameters for the most common types of covalent bonds formed by C, N, O, H atoms were derived[36,37] and implemented in the WinXPRO software package,[38,39] which uses the electron density characteristics obtained from high-precision X-ray diffraction intensities. Successful applications of such a parametric model for estimation of the bond order have been published.[40–43] To further develop this approach, we can use the electron delocalization indices[33,44] as reference values. These descriptors are used to measure the exchange-correlation interaction of electrons belonging to two adjacent atomic basins A and B with a common QTAIM zero-flux surface. In the single-determinant approximation for the many-electron wave function, the electron delocalization index DI(A–B) determines the number of electrons distributed between atomic basins A and B:

$$\mathrm{DI(A-B)} = 4\sum_{i,j=1}^{n_{occ}} S_{ij}(\mathrm{A})S_{ij}(\mathrm{B}), \quad (1)$$

$$S_{ij}(\mathrm{A}) = \int_{\mathrm{A}} \chi_i(r)\chi_j(r)\mathrm{d}r. \quad (2)$$

Here S_{ij}(A) are the elements of the atomic overlap matrix determined in terms of molecular orbitals χ_i and χ_j; integration is carried out over the Bader atomic basin; the summation in equation (1) is performed over all occupied molecular orbitals.

We aim to develop a bond order model suitable for S–N, S–C and S–S bonds in 1,2,3-dithiazoles and other N,S-heterocycles. Therefore, we analyze the electron delocalization indices DI(A–B) in N,S-heterocycles and choose the fitting parameters in the equation based on the QTAIM characteristics of electron density for each type of the mentioned covalent bonds. In addition, we compare the topological bond orders in 1,2,3-dithiazoles with Pauling's orders. Finally, we test the concept of turning atomic radii to establish a reliable and straightforward parametric model for estimating bond order.

In our sample, the calculated electron delocalization indices DI(S–S) range from 0.962 to 1.352 [Figure 1(*a*)]. The highest value has a simple S–S bond in dimethyl disulfide. In neutral 1,2,3-dithiazoles or 1,2,3,5-dithiadiazoles, the DI(S–S) values are lower than in their cations. In turn, they are higher in 1,2,3-dithiazoles than in 1,2,3,5-dithiadiazoles. The minimum DI(S–S) index is observed in the dimerization product [Figure 2(*a*) and Table S1, entry 21]. In this compound, adjacent dithiazole rings open and form two thionic groups that stabilize the planar molecule with two intramolecular chalcogen bonds (ChB) S···S–S···S. Thus, if both sulfur atoms act as ChB donors, the S–S bond is much weaker. Interestingly, if the sulfur atom participates in intramolecular interactions only as a nucleophile, the DI(S–S) values are higher. All these observations are in good agreement with the previously drawn conclusion: the loss of electron density in divalent sulfides can lead to the formation of centers of trivalent sulfur.[17]

In 1,2,3-dithiazolium cations, the delocalization indices of the S–C bond are higher than in electrically neutral 1,2,3-dithiazoles. In cations, DI(S–C) ranges from 1.310 to 1.404. The highest value is observed for the Appel's salt cation [Figure 3(*a*)]. Thus, in the 1,2,3-dithiazole ring, the S–C bond is not formally a double bond; the bond order is close to the order of the sesquialteral bond. Note that in the electrically neutral 5*H*-1,2,3-dithiazole-5-thione (Table S1, entry 35), we see relatively high DI values for both the thione C=S bond (1.694) and the single S–C bond (1.290). Since our sample includes heterocycles with thiol and thione fragments, we have a wide range of electron delocalization indices for S–C bonds: from 0.976 to 1.828 [Figure 1(*b*)]. The exocyclic thione group demonstrates the highest DI(S–C); however, it is below the values expected for a typical double bond. We attribute this to the conjugation effects in the considered heterocycles. However, the complete alignment of the delocalization indices for the adjacent S–C and C=S bonds does not occur. Comparing DI(S–C) for five successive S–C bonds in 2-(*tert*-butylthio)-4,4-dimethylthiazole-5(4*H*)-thione [Figure 2(*b*) and Table S1, entry 40], we see that the endocyclic S–C bond adjacent to the thione group exhibits a higher DI(S–C) compared to that of the endocyclic S–C bond adjacent to the thioether group. This observation indicates that the alignment of bond orders in the S–C=S fragment is not perfect.

The electron delocalization indices DI(S–N) range in our sample from 1.070 to 1.462 [Figure 1(*c*)]. For 1,3,2-dithiazoles, the DI(S–N) values are usually lower than for 1,2,3,5-dithidiazoles but higher than for 1,2-thiazoles and 1,2,5-thiadiazoles. For cations, the DI(S–N) values are higher than for electrically neutral molecules. Thus, the DI indices of S–S, S–C and S–N bonds differ significantly in cations and neutral molecules; they are also sensitive to the effects of conjugation and substitution in heterocycles.

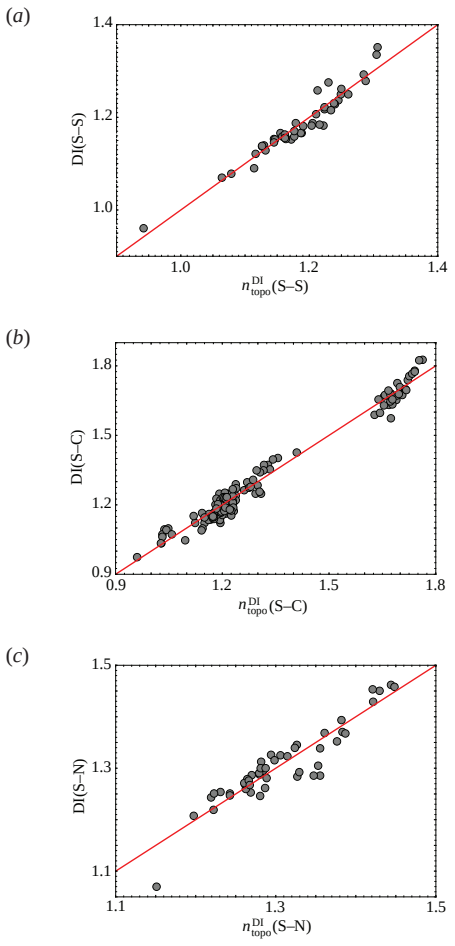


Figure 1 Reference delocalization indices and predicted topological bond orders for covalent bonds in five-membered N,S-heterocycles: (*a*) S–S bonds, (*b*) S–C bonds and (*c*) S–N bonds.

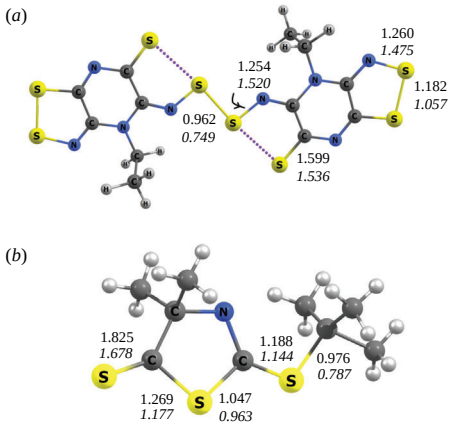


Figure 2 Predicted bond orders for molecules with (*a*) intramolecular chalcogen bonds and (*b*) adjacent S–C bonds. The top number is the topological bond order n^{DI}_{topo} predicted by equation (3); the bottom number in italics is the bond order n^{DI} predicted by equation (1).

To predict the topological bond orders n^{DI}_{topo} in five-membered N,S-heterocycles, we assumed that n^{DI}_{topo} is equal to DI(A–B) and used the following equation:

$$n^{DI}_{topo} = a_0 + a_1[\lambda_1(r_b) + \lambda_2(r_b)] + a_2\lambda_3(r_b) + a_3\rho(r_b). \quad (3)$$

Using the electron delocalization indices DI(S–X) (X = S, C and N) (Figure 1) as reference values in equation (3), we obtained parameter sets for the S–S, S–C and S–N bonds (Table 1).

Next, we turned to Pauling's scheme,[18] which estimates the bond order p(A–B) as follows:

$$p(A–B) = \exp[(r^{cov}_A + r^{cov}_B - R_{AB})/0.3]. \quad (4)$$

Here r^{cov}_A is the revised covalent radius,[45] and R_{AB} is the interatomic distance. At the first stage, we used the same parameter in the denominator of the exponent for all types of bonds. For dithiazolium rings, the Pauling bond order p(S–S) is in the range of 1.15 ± 0.07. For 1,2,3-dithiazoles, the p(S–S) value is lower: 0.96 ± 0.05. Thus, between cations and neutral heterocycles, the difference in the p(S–S) indices has the same tendency as the difference in the electron delocalization indices DI(S–S). The maximum p(S–C) value for the thione group does not exceed 1.700, which is lower than the expected value, even if we consider conjugation effects. For example, for the thione bond in electrically neutral 5*H*-1,2,3-dithiazole-5-thione, p(S–C) is 1.571, and for the typical single S–C bond in the cycle, p(S–C) is 1.119. The p(S–N) bond orders predicted from interatomic distances are, on average, higher than the topological bond orders. This discrepancy may be due to the systematically low $\rho(r_b)$ values for the S–N bond in substituted or fused dithiazoles. In contrast, the S–C bonds had electron delocalization indices DI(S–C) that exceed the corresponding Pauling bond orders p(S–C).

It follows that in 1,2,3-dithiazoles, the actual electron delocalization for S–N bonds is lower than expected based on their bond lengths; as a result, the bond order here is close to the single bond order. However, the discrepancy between the electron delocalization indices and bond orders can also occur due to insufficient parameters in equation (4), which do not take into account the hybridization of atoms in the heterocycles under consideration. In turn, there is a possibility that the electron density is partially shifted from the sulfur atomic basin to the S–C bond; as a result, the S–C bond acquires a higher bond order without a characteristic shortening of the bond length.

Table 2 The parameters of equation (5) for the bond order n^{DI}_{turn} based on the scale of turning radii,[19] the maximum and minimum n^{DI}_{turn} values for a specific bond type, the correlation coefficients R and the differences between the topological bond orders n^{DI}_{topo} and n^{DI}_{turn}.

Bond	a_1	a_2	n^{DI}_{turn}(min)	n^{DI}_{turn}(max)	R	Δ_{min}	Δ_{max}
S–S (36)	0.125	0.567	0.990	1.297	0.95	–0.06	0.03
S–C (134)	0.015	0.326	0.855	1.737	0.97	–0.14	0.12
S–N (40)	0.192	0.672	1.163	1.435	0.91	–0.04	0.04

To test this hypothesis, we re-parametrized Pauling's equation using the electron delocalization indices as a reference in equation (5) by analogy with the topological bond orders n^{DI}_{topo}. To reduce the dependence of the model on the type of atomic hybridization, since this is not *a priori* obvious for the 1,2,3-dithiazole system, we tested the turning radii instead of the covalent radii commonly used in equation (4):

$$n^{DI}_{turn} = a_1\exp[(r^{turn}_A + r^{turn}_B - R_{AB})/a_2]. \quad (5)$$

Here r^{turn}_A and r^{turn}_B are the turning radii of neutral atoms: r^{turn}(C) = = 1.49 Å, r^{turn}(N) = 1.24 Å and r^{turn}(S) = 1.68 Å.[19] R_{AB} is the interatomic distance, and a_1 and a_2 are fitting parameters. As a result, improved statistical characteristics of the bond orders n^{DI}_{turn} were obtained. Fitted parameters and correlation coefficients for DI(A–B) and n^{DI}_{turn} are given in Table 2.

Taking several 1,2,3-dithiazole systems as examples (Figure 3), we compared the bond orders in cations, electrically neutral molecules and the triplet states of electrically neutral molecules. The latter are the radicals in our sample. We also checked how the n^{DI}_{topo} and n^{DI}_{turn} values correlate. Some discrepancies between n^{DI}_{topo} and n^{DI}_{turn} values (Table 2) were observed for S–C bonds. As a rule, in cations n^{DI}_{turn} is higher than n^{DI}_{topo}; nevertheless, the situation is opposite in electrically neutral molecules. This fact means that the electron density remains relatively low for the short S–C bond in the cation, reflecting a high n^{DI}_{turn}. Interestingly, for S–N bonds, the n^{DI}_{topo} and n^{DI}_{turn} values correlate well for all electronic states of the molecules.

Both n^{DI}_{topo} and n^{DI}_{turn} indices indicate that the S–S bond order in the 1,2,3-dithiazolium cation [Figure 3(*a*)] is slightly greater than one and is close to the usual single bond in dimethyl disulfide (Table S2). The lowest S–S bond orders are observed for the triplet states of fused heterocycles [Figures 3(*d*),(*e*)]. The resulting bond orders are much higher for S–C and S–N bonds in cations; they are also close to each other in magnitude. Compared to cations, the S–C and S–N bond orders in triplet states [Figures 3(*d*),(*e*)] differ more strongly. At the same time, in the electrically neutral bis-dithiazole [Figure 3(*b*)] and tetrathiadiazafulvalene [Figure 3(*c*)], the S–C bond orders are low and approximately equal to or lower than those of the S–S bonds. It can be assumed that the most pronounced difference between electrically neutral 1,2,3-dithiazoles and 1,2,3-dithiazolium cations is associated with the features of the electron density of the corresponding S–C bonds. The electronic configuration with the double S–C bond corresponds to the formal charge +1, often attributed to sulfur in the heterocycles under consideration, and the elevated

Table 1 The parameters of equation (3) for the topological bond order n^{DI}_{topo}, its maximum and minimum values for a specific bond type and the correlation coefficients R between the predicted n^{DI}_{topo} and DI(A–B). The number of bonds in the samples is indicated in parentheses.

Bond	a_0	a_1	a_2	a_3	R	n^{DI}_{topo}(min)	n^{DI}_{topo}(max)
S–S (36)	–0.11±0.15	5.53±0.89	–0.23±0.52	22.22±2.3	0.97	0.912	1.310
S–C (134)	–0.24±0.07	1.38±0.09	0.34±0.07	10.62±0.25	0.99	0.975	1.783
S–N (40)	0.21±0.19	–0.20±0.18	0.08±0.06	4.02±1.11	0.94	1.148	1.452

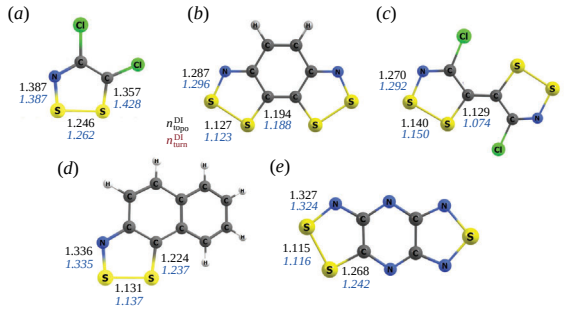


Figure 3 Predicted bond orders for (*a*) 4,5-dichloro[1,2,3]dithiazol-2-ium cation (Appel's salt), electrically neutral molecules (*b*) benzo[1,2-*d*:4,3-*d'*]-bis[1,2,3]dithiazole and (*c*) *trans*-4,4′-dichlorobi[[1,2,3]dithiazol-5-ylidene], as well as triplet states of radicals (*d*) 3*H*-naphtho[2,1-*d*][1,2,3]-dithiazol-3-yl and (*e*) 3*H*-[1,2,3]dithiazolo[4,5-*b*][1,2,5]thiadiazolo[3,4-*e*]-pyrazin-3-yl. The top number is the topological bond order n_{topo}^{DI} predicted by equation (3); the bottom number in italics is the bond order n_{turn}^{DI} predicted by equation (5) based on turning radii.

bond orders n_{topo}^{DI} and n_{turn}^{DI} in cations are consistent with this tradition.

In the 1,2,3-dithiazolium cations or radicals, the difference in the bond orders of the neighboring S–S and S–C bonds is noticeably higher than in the electrically neutral structures in Figure 3. This fact indicates a more uniform delocalization of electrons in 1,2,3-dithiazole cycles condensed with aromatic fragments, in contrast to 1,2,3-dithiazolium systems, where the alternation of bond orders for the S–C, S–S and S–N bonds is more pronounced.

Thus, for S–C, S–N and S–S bonds in substituted or fused 1,2,3-dithiazole systems, we re-parameterized the QTAIM-based (topological) bond order model and Pauling's equation, using the electron delocalization indices calculated for a large sample of five-membered N,S-heterocycles as a reference. It was shown that the turning radii of atoms, which do not depend on the type of atomic hybridization, can be successfully applied to evaluate the Pauling bond orders instead of the sum of covalent radii. Both models show that the S–C, S–N and S–S bond orders differ in cations, radicals and electrically neutral 1,2,3-dithiazole-based systems, and they are sensitive to the effects of conjugation and substitution in these heterocycles. The alternation of bond orders for S–C, S–S and S–N bonds is more pronounced in cations, and their values are higher than for electrically neutral systems.

As a result, we recommend the topological bond order model to quickly estimate bond orders using electron density derived from high-precision X-ray diffraction data measured for sulfur-containing molecular systems to understand better the features of electron distribution in five-membered N,S-heterocycles.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.09.029.

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