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# Probing the aromaticity of bis(diazolo)pyrazine radical anions

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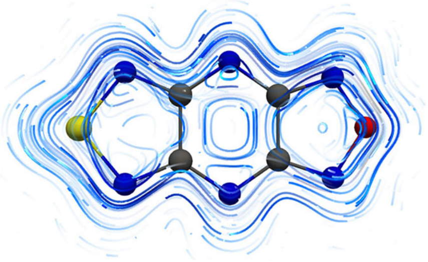
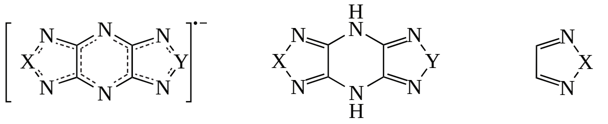
**The aromaticity of a series of heterocyclic radical anions of bis(diazolo)pyrazine type, $X(CN)_2N_2(CN)_2Y$ (X, Y = O, S, Se, Te) was explored by the methods of electron density of delocalized bonds (EDDB) and gauge-included magnetically induced currents (GIMIC). The existence of π-aromaticity that encloses the entire molecule, which was due to delocalization of seven β-electrons, was shown. The degree of aromaticity depends on the nature of the X(Y) heteroatom and varies in the series S > O > Se > Te.**



*Keywords*: bis(diazolo)pyrazines, radical anions, molecular magnet, open shell aromaticity, aromaticity degree, quantum chemical calculations.

Stable organic radicals are important compounds[1–3] in terms of both reactivity and applicability.[1–7] In particular, high-stability heterocyclic radicals show promise for magnetic devices,[4] memory cells,[8–10] components of organic spintronics,[11–13] spin sensors[14] and spin filters.[15,16] As shown previously, bis(furazano)pyrazine radical anion **1** (Figure 1) has remarkable stability and promising magnetic properties.[17] Its ESR spectrum reveals that spin and, hence, electron density is delocalized over all the atoms,[17] so the π-conjugated system in **1** can be assumed to have an aromatic character. Since an almost complete series of precursors **11–18** was reported previously,[18–24] it is of interest to perform a comparative analysis of the entire series of structures **1–10**.

Polycyclic aromatic systems are of interest in terms of aromaticity as well as the development of the theory and methodology.[25,26] The classical rules of aromaticity, the Hückel rule ($4n+2$ electrons), the Baird rule ($4n$ electrons) and the Clar rule (the rule of aromatic π-sextets) are not applicable to polycyclic systems, especially to those which contain heteroatoms and/or are radical cations or anions, although both aromatic and antiaromatic radicals do exist.[25,27–31]



**1** X = Y = O
**2** X = O, Y = S
**3** X = O, Y = Se
**4** X = O, Y = Te
**5** X = Y = S
**6** X = S, Y = Se
**7** X = S, Y = Te
**8** X = Y = Se
**9** X = Se, Y = Te
**10** X = Y = Te

**11** X = Y = O
**12** X = O, Y = S
**13** X = O, Y = Se
**14** X = O, Y = Te
**15** X = Y = S
**16** X = S, Y = Se
**17** X = S, Y = Te
**18** X = Y = Se
**19** X = Se, Y = Te
**20** X = Y = Te

**21** X = O
**22** X = S
**23** X = Se
**24** X = Te

**Figure 1** The molecules studied.

In this work we present the results of studying the aromaticity in the series of radical anions **1–10** using the most advances computed aromaticity criteria, *i.e.* the methods of electron density of delocalized bonds (EDDB)[32] and gauge-included magnetically induced currents (GIMIC),[33] in comparison with the starting bis(diazolo)pyrazines **11–20** and diazoles **21–24**. The calculations presented here were performed at PBE0/aug-cc-pVTZ theory level, while the aug-cc-pVTZ-pp basis set was used for Te (see Online Supplementary Materials for details). The knowledge of the pattern of how the aromatic properties of **1–10** vary would make it possible to fine-tune the magnetic properties in the molecular design of devices based on these compounds.

Each of neutral tricycles **11–20** formally contains sixteen π-electrons. Obviously, this configuration might result in antiaromaticity, whereas the diazole ring in them comprise and separately (**21–24**) contains six π-electrons, *i.e.* it should be aromatic. The results on the EDDB and GIMIC criteria (see Online Supplementary Materials, Table S1) confirm the π-aromatic nature of structures **21–24**. The number of efficiently delocalized π-electrons (the π-$EDDB_H$ value) varies within 2.09–3.36, while the ring current (IRCS) varies within 10.6–13.4 nA $T^{-1}$. Despite the variation in the ring size and the presence of heteroatom X, both criteria give the same expected order of increasing aromaticity: Te (**24**) < Se (**23**) ⩽ O (**21**) < S (**22**).

Though tricyclic bis(diazolo)pyrazines **11–20** contain sixteen π-electrons corresponding to antiaromaticity, they have planar structures and are thermally stable.[18] The EDDB results for **11–20** (see Online Supplementary Materials, Tables S2, S3 and Figure S1) show π-type delocalization involving all the atoms. The IC distribution in tricycles **11–20** (Figures 2 and S2) looks like an IC superposition of two aromatic diazole rings, *i.e.* there are two diatropic local currents of five-membered rings but no global ring current enclosing all the three rings. A rather strong paratropic ring current is discernible in the six-membered ring. As a result, the IRCS value of the five-membered ring varies

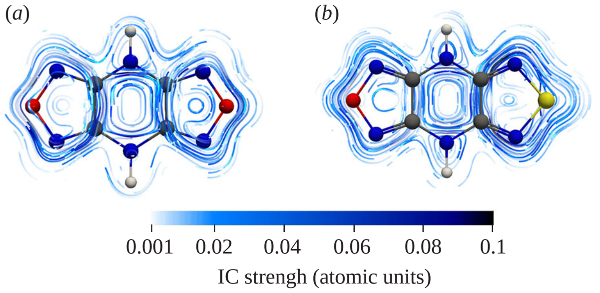


**Figure 2** Maps of IC lines for (*a*) structure **11** and (*b*) structure **12** at a distance of 0.25 Å above the molecule plane.

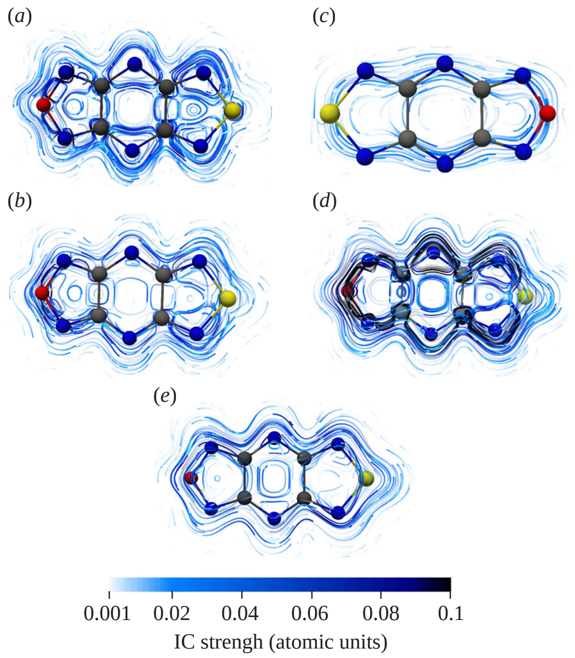


**Figure 3** Maps of IC lines for **2** (X = O, Y = S): (*a*) α-contribution, (*b*) β-contribution, (*c*) spin density contribution, (*d*) total IC density, (*e*) total IC density arranged at a distance of 0.25 Å above the molecule plane.

within 8.7–9.6 nA T$^{-1}$ (see Table S2), whereas the paratropic ring current of the six-membered ring is very weak (–0.5 to –2.7 nA T$^{-1}$). Thus, the conjugation system of π-electrons in **11**–**20** avoids antiaromaticity and forms two π-aromatic diazole rings conjugated *via* two NH-bridges. The aromaticity degree in each five-membered ring does not depend on the second five-membered ring, and what is more, it is smaller than that in the corresponding monocyclic diazoles **21**–**24**.

As radicals **1**–**10** are formed from molecules **11**–**20**, one π-electron is withdrawn from the π-conjugation system. In fact, the EDDB criterion shows that radical anions **1**–**10** have a larger degree of conjugation than bis(dithiazolo)pyrazines **11**–**20**: for example, the π-EDDB$_H$ values are larger by 2 ē on average (Table 1). The current values (see Online Supplementary Materials, Table S4) also confirm it, the IRCS value of the six-membered ring increases by ~4 nA T$^{-1}$, whereas the IRCS of the diazole ring increases by ~3 nA T$^{-1}$. Fifteen π-electrons that are conjugated in **1**–**10** fail to meet any of the aromaticity rules, so we analyzed EDDB and GIMIC data for the contributions of α- and β-electrons separately (see Tables 1 and S4, S5). The π-EDDB$_H$ and π-EDDB$_F$ values for the α-contribution is smaller by ~1.5 ē than those for the β-contribution. The high population of β-NODB1–7 (> 0.7 ē) and the very small β-NODB8 (~0.13 ē) (see Table S5) indicate that seven β-electrons are delocalized. The increase in the π-EDDB$_H$ value in **1**–**10** in comparison with **11**–**20** is mainly due to the involvement of nitrogen atoms of the pyrazine ring that is observed as an increase in the π-EDDB$_F$ value for this ring by ~1 ē. Aromaticity can be distinguished from strong conjugation by the existence of net diamagnetic ring current. Radicals **1**–**10** in comparison with molecules **11**–**20** show a global diatropic ring current over all the three rings [Figures S5 and 3(*e*)]. The map of spin density IC lines [Figures S6 and 3(*c*)] shows that the induced current flow outside the rings change direction. This occurs because the diatropic currents of β-density [Figure 3(*b*)] are stronger than those of α-density. At the same time, the distribution of α-IC [Figure 3(*a*)], in which strong paramagnetic currents within the ring and strong local currents around certain bonds and unshared pairs are observed, matches a conjugated but non-aromatic molecule. Thus, EDDB and GIMIC data demonstrate that the aromatic nature of **1**–**10** is due to delocalization of seven β-electrons.

In essence, the ‘$4n+2$ π-electrons’ Hückel’s rule for π-aromaticity means that $4n+2$ electrons occupy $2n+1$ bonding orbitals, so it can be reformulated as the ‘$2n+1$ occupied orbitals’ rule. It is then obvious that the seven β-electrons that cause the aromaticity of **1**–**10** are arranged on seven β-orbitals and satisfy the ‘$2n+1$ occupied orbitals’ rule with $n = 3$.

Apparently, the aromaticity of radicals **1**–**10** is weaker than that of **21**–**24** (a comparison with classical heterocycles and arenes is presented in the Online Supplementary Materials). Comparison of heterocycles **1**–**10** shows that EDDB and GIMIC data vary considerably due to changes in the size of the five-membered ring and because the conjugation system is tricyclic. The values of π-EDDB and IRCS qualitatively show that conjugation is non-uniform in the rings and is higher in the five-membered ring. The degree of aromaticity/conjugation depends on the nature of heteroatoms X and Y. It is relevant to compare the aromaticity in the series **1**–**10** based on the π-EDDB$_H$ value

**Table 1** Values of π-EDDB (ē) for structures **1**–**10** calculated at PBE0/aug-cc-pVTZ level.

| Structure | X | Y | π-EDDB$_H$/ē | | | π-EDDB$_F$/ē | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | XN$_2$C$_2$ | | | C$_4$N$_2$ | | | C$_2$N$_2$Y | | |
| | | | α | β | total | α | β | total | α | β | total | α | β | total |
| **1** | O | O | 4.00 | 5.85 | 9.85 | 0.95 | 1.62 | ***2.56*** | 2.11 | 2.61 | **4.72** | 0.95 | 1.62 | ***2.56*** |
| **2** | O | S | 3.87 | 5.38 | 9.26 | 1.35 | 2.29 | 3.63 | 1.97 | 2.38 | 4.35 | 1.62 | 2.21 | 3.83 |
| **3** | O | Se | 3.72 | 5.60 | 9.33 | 1.36 | 2.35 | 3.71 | 1.88 | 2.50 | 4.37 | 1.51 | 2.33 | 3.84 |
| **4** | O | Te | 2.63 | 5.59 | 9.22 | 1.39 | 2.37 | 3.76 | 1.84 | 2.53 | 4.37 | 1.41 | 2.28 | 3.69 |
| **5** | S | S | 4.27 | 5.77 | **10.04** | 2.13 | 2.59 | **4.74** | 1.65 | 2.39 | ***4.04*** | 2.13 | 2.59 | **4.74** |
| **6** | S | Se | 4.06 | 5.51 | 9.57 | 1.68 | 2.31 | 4.00 | 2.01 | 2.46 | 4.47 | 1.48 | 2.25 | 3.73 |
| **7** | S | Te | 3.99 | 5.34 | 9.33 | 1.72 | 2.27 | 3.99 | 1.96 | 2.37 | 4.33 | 1.40 | 2.16 | 3.56 |
| **8** | Se | Se | 3.85 | 5.60 | 9.46 | 1.50 | 2.31 | 3.91 | 1.90 | 2.55 | 4.45 | 1.50 | 2.31 | 3.91 |
| **9** | Se | Te | 3.72 | 5.49 | 9.21 | 1.50 | 2.30 | 3.81 | 1.84 | 2.49 | 4.33 | 1.39 | 2.21 | 3.61 |
| **10** | Te | Te | 3.67 | 5.43 | ***9.10*** | 1.42 | 2.23 | 3.65 | 1.83 | 2.49 | 4.31 | 1.42 | 2.23 | 3.65 |

(see Table 1), while analysis of IRCS values (see Online Supplementary Materials, Table S4) should take its dependence on the ring size into account. Comparison of symmetric molecules **1**, **5**, **8** and **10** shows that the aromaticity degree according to the $\pi$-EDDB$_H$ value in the series of heteroatoms X/Y changes in the same expected series as in the monocyclic diazoles **21**–**24**: Te (**10**) < Se (**8**) < O (**1**) < S (**5**). At the same time, the IRCS values for the X–N bonds (see Table S4) nearly do not change (~10 nA T$^{-1}$). Desymmetrization of **1**, **5** and **8** due to incorporation of heavier Y atoms results in a decrease in the $\pi$-EDDB$_H$ value: the effect is stronger if X = O and decreases toward X = S and Se. In general, the IRCS values of X–N and Y–N bonds also agree with this. The effect of X–N bond polarity reversal from X = O to X = S, Se and Te manifests itself on comparison of **1**–**4**. Along with the decrease in the overall delocalization effect from **1** to **4** (a decrease in $\pi$-EDDB$_H$ from 9.82 to 9.22 $\bar{e}$), the delocalization in the $ON_2C_2$ ring increases, which is observed as an increase in $\pi$-EDDB$_F$ by more than 1 $\bar{e}$ and an increase in IRCS for the O–N bond in **1**–**4** from 9.9 to 10.7 nA/T. The delocalization in the two other rings becomes weaker and the $\pi$-EDDB$_F$ values decrease by ~0.4 and 0.3–1.0 $\bar{e}$ for the $C_4N_2$ and $C_4N_2Y$ rings, respectively.

The study of the aromaticity of polycyclic radicals is a challenging task. This work demonstrated the application of two most advanced and powerful criteria, GIMIC and EDDB. The values of these criteria for **1**–**24** agree qualitatively and quantitatively, provided that two conditions are met, *i.e*. the ring size and tricyclic structure are taken into consideration, whereas a single aromaticity criterion is insufficient. It has been shown that removal of one electron from the 16 $\pi$-electron delocalization system of bis(diazolo)pyrazines **11**–**20**, which avoid anti-aromaticity and form two aromatic diazolium rings bound with conjugation *via* two NH-bridges, results in the formation of tricyclic $\pi$-aromaticity in **1**–**10** caused exclusively by the delocalization of seven $\beta$-electrons. Comparison of $\pi$-aromaticity in the series **1**–**10** shows that its degree depends on the heteroatom X and agrees with the traditional understanding, S > O > Se > Te, in the case of symmetric molecules **1**, **5**, **8** and **10**. Desymmetrization of these molecules by incorporation of a heteroatom Y that is heavier than X results in a decrease in $\pi$-aromaticity. Thus, controlling the degree of aromaticity in compounds **1**–**10** by incorporating a required heteroatom would make it possible to finely tune the properties of devices and their components based on the radical anions studied.

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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.2022.11.008.

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