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Supramolecular organic frameworks derived from bromoaryl-substituted dichlorodiazabutadienes *via* Cl···Br halogen bonding

Namiq G. Shikhaliyev,[a] Abel M. Maharramov,[a] Khanim N. Bagirova,[a] Gulnar T. Suleymanova,[a] Biligma D. Tsyrenova,[b] Valentine G. Nenajdenko,*[b] Alexander S. Novikov,[c] Victor N. Khrustalev[d,e] and Alexander G. Tskhovrebov*[d,f]

[a] *Baku State University, AZ-1148 Baku, Azerbaijan*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. E-mail: nenajdenko@gmail.com*
[c] *St. Petersburg State University, 199034 St. Petersburg, Russian Federation*
[d] *Peoples Friendship University of Russia (RUDN University), 117198 Moscow, Russian Federation*
[e] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[f] *N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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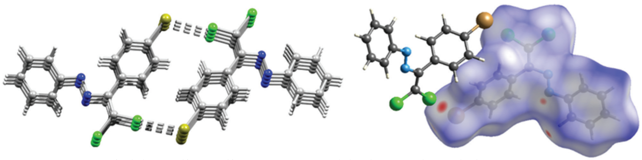
1-Aryl-3-(4-bromophenyl)-4,4-dichloro-1,2-diazabuta-1,3-dienes were synthesized *via* copper-catalyzed reaction of 4-bromobenzaldehyde arylhydrazones with CCl_4. X-ray diffraction analysis revealed non-covalent Cl···Br interactions in the crystalline state and formation of 3D supramolecular framework; DFT calculations and topological analysis of the electron density distribution within the framework of Bader's theory (QTAIM method) confirmed these observations. Theoretical calculations showed that highly polarizable dichlorodiazadiene unit is capable of acting as a relatively strong halogen bond donor.

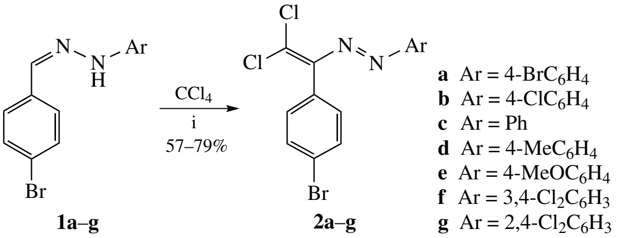


Dichlorodiazadienes – novel halogen bond donors

Keywords: non-covalent interactions, crystal engineering, halogen bonding, azo dyes, DFT, QTAIM.

Self-assembly is a convenient approach for the creation of supramolecular architectures with various functions, which are often not shown by the corresponding monomers.[1] The possibility of fine control of the local molecular environment is highly desirable to access new properties for substances that function as catalysts, luminescent or conductive materials, *etc*.[2–4] Halogen bonding has recently emerged as useful instrument for the accurate control of the structural organization of such supramolecular materials. In this context, halogen–halogen interactions received a particular attention and were intensively explored both experimentally and theoretically.[5,6] Recently, we found novel dichlorodiazadienes which can be easily prepared by the reaction between CCl_4 and arylated hydrazones (Scheme 1).[7] These compounds demonstrated very interesting properties.[8–13]

Following our interest in non-covalent interactions,[14–23] here we describe the synthesis and characterization of novel halogenated dichlorodiazadienes. Non-covalent Cl···Br interactions were detected in the crystalline state and studied theoretically by DFT calculations, QTAIM analysis and Hirshfeld surface analysis. Calculations demonstrated that highly polarizable dichlorodiazadiene unit is capable of acting as a relatively strong halogen bond donor. When the dye was decorated with halogen bond-accepting bromine atoms, formation of 3D supramolecular framework was observed.



Scheme 1 *Reagents and conditions*: i, CCl_4, CuCl (cat.), TMEDA, DMSO, room temperature, 1–3 h.

Desired dichlorodiazadienes **2a–g** were easily prepared *via* copper-mediated reaction between hydrazones **1a–g** and CCl_4 and isolated in high yields as red solids. The structure of **2a–g** was confirmed by the ^1H and ^{13}C NMR spectroscopy, and X-ray diffraction analysis for **2a** and **2c** (Figure 1, see also Online Supplementary Materials, Table S1 and Figure S3). Suitable for X-ray study single crystals of **2a** and **2c** were obtained by recrystallization from dichoromethane/hexane.[†] In general, metrical parameters for **2a** and **2c** are close to those found for earlier described dichlorodiazadienes and other azo compounds.[8,18–23] Remarkably, decoration of dye backbone with

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[†] *Crystal data for* **2a**. A colourless prismatic crystal [$C_{14}H_8N_2Cl_2Br_2$ (M_r = 434.92)] is monoclinic, space group $P2_1$, at T = 100 K, a = 9.861(2), b = 4.0147(8) and c = 18.472(4) Å, β = 95.29(3)°, V = 728.2(3) Å^3, Z = 2, d_{calc} = 1.984 g cm^{-3}, $F(000)$ = 420, μ = 7.635 mm^{-1}. 12738 reflections (3191 independent reflections, R_{int} = 0.070) were measured and used in the refinement. The refinement converged to R_1 = 0.053 for 2718 observed reflections with $I > 2\sigma(I)$ and wR_2 = 0.133 for all independent reflections, S = 1.069.

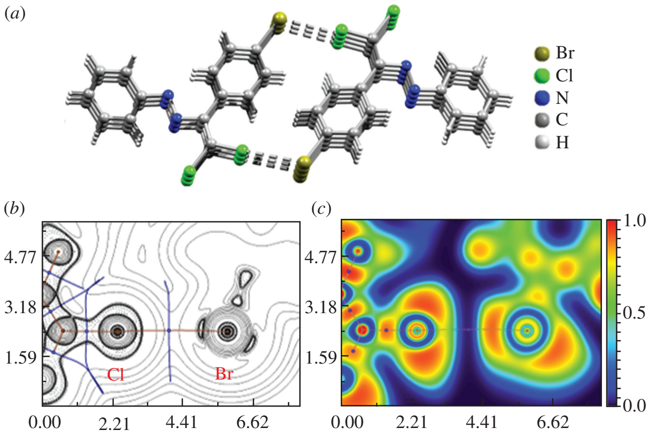

Figure 1 (*a*) Ball-and-stick representation of the structure of **2c** in the crystal, (*b*) contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$ and (*c*) visualization of electron localization function (ELF) analysis for halogen bonds Cl···Br in **2c**.

bromine atoms had a dramatic impact on its organization in the solid state. In the crystal of **2c**, molecules form columns *via* π–π interactions of the aromatic rings. Each column interacts with the neighboring one *via* Cl···Br attractive interactions to form dimers of columns which form spiralic 1D supramolecular polymer (see Figure 1). Introduction of another bromine atom into dichlorodiazadiene molecule (compound **2a**) does not break helical dimers of columns. In addition to that, the dimers would coordinate to the neighboring dimers *via* Cl···Br interactions to form supramolecular organic framework (see Figure S3).

To understand the nature and quantify energies of halogen bonds Cl···Br in compounds **2a** and **2c**, the DFT calculations followed by the topological analysis of the electron density distribution within the QTAIM approach[27] were carried out at the ωB97XD/6-311++G** level of theory for model supramolecular associates (see Online Supplementary Materials for computational details and Table S1). Results of QTAIM analysis are summarized in Table S2, the contour line diagrams of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces as well as visualization of electron localization function (ELF) analysis for halogen bonds Cl···Br in **2a** and **2c** are shown in Figures 1 and S1. Visualization of electrostatic surface potential distribution in isolated molecules **2a** and **2c** with selected $V_{\mathrm{s,max}}$ and $V_{\mathrm{s,min}}$ values on halogen atoms corresponding to σ-holes and electron density 'belts', respectively, is presented in Figure S2.

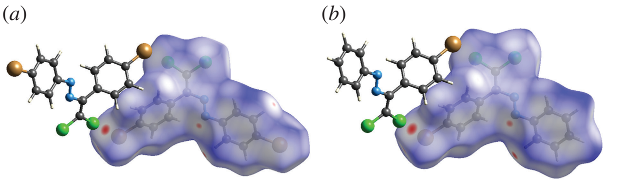

Figure 2 Visualization of Hirshfeld surfaces for X-ray (*a*) structure **2a** and (*b*) structure **2c**.

The QTAIM analysis of model supramolecular associates demonstrates the presence of bond critical points (3, –1) for halogen bonds Cl···Br in **2a** and **2c** (see Table S2). The low magnitude of the electron density (0.006–0.008 a.u.), positive values of the Laplacian of electron density (0.022–0.031 a.u.), and very close to zero positive energy density (0.001–0.002 a.u.) in these bond critical points (3, –1) are typical of halogen–halogen noncovalent interactions.[28] The balance between the potential and kinetic energy densities of electrons at the bond critical points (3, –1) for halogen bonds Cl···Br in **2a** and **2c** reveals the absence of covalent contribution in these interactions.[29] The $\lambda_2 < 0$ reveals that halogen bonds Cl···Br in **2a** and **2c** are attractive[30,31] (see Table S2). Overall, it follows from the results of theoretical calculations that halogen bonds Cl···Br in **2a** and **2c** are similar in terms of energies (their estimated strength per one contact is only 1–2 kcal mol^{-1}), which correlates well with close values of maximal and minimal electrostatic surface potentials ($V_{\mathrm{s,max}}$ and $V_{\mathrm{s,min}}$) on halogen atoms in isolated molecules **2a** and **2c** (Figure S2). To understand what kind of interatomic contacts gives the largest contributions in crystal packing, we carried out the Hirshfeld surface analysis for X-ray structures of **2a** and **2c** (Table S3 and Figure 2).

In summary, we have synthesized new halogenated dichlorodiazadienes, accomplished their full characterization, while for two of them single crystal X-ray analysis was performed. Crystal structures exhibited multiple Cl···Br interactions, which were analyzed by DFT calculations and topological analysis of the electron density distribution within the framework of Bader's theory (QTAIM method) and Hirshfeld surface analysis.

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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.2021.03.015.

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Crystal data for **2c**. A colourless prismatic crystal [$C_{14}H_9N_2Cl_2Br$ (M_r = 356.03)] is monoclinic, space group $P2_1/n$, at T = 100 K, a = 9.937(2), b = 3.9990(8) and c = 33.852(7) Å, β = 94.09(3)°, V = 1341.8(5) Å^3, Z = 4, d_{calc} = 1.762 g cm^{-3}, $F(000)$ = 704, μ = 4.450 mm^{-1}. 27172 reflections (3078 independent reflections, R_{int} = 0.084) were measured and used in the refinement. The refinement converged to R_1 = 0.040 for 2532 observed reflections with $I > 2\sigma(I)$ and wR_2 = 0.102 for all independent reflections, S = 1.043.

X-ray diffraction data were collected on the 'Belok' beamline (λ = 0.78790 Å) at the National Research Center 'Kurchatov Institute' (Moscow, Russian Federation) using a Rayonix SX165 CCD detector and corrected for absorption using the Scala program.[24] The data were indexed, integrated and scaled using the utility iMOSFLM in CCP4 program.[25] The structures were determined by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [$U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$]. The calculations were carried out using the SHELXTL program.[29,30]

CCDC 2043048 (**2a**) and 2043049 (**2c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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