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2-DIETHYLAMINOVINYL DERIVATIVES OF HALOGENATED 1,4-QUINONES: SYNTHETIC AND STRUCTURAL ASPECTS

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Diethylaminovinyl derivatives of halogenated 1,4-quinones (enaminoquinones) are produced by the interaction of halogenated 1,4-quinones with *N*,*N*-diethyl-*N*-vinylamine obtained in situ from Et_2NH and MeCHO. Molecular and crystal structures of enaminoquinones halogenated in the quinone fragment are determined. It is shown that in the solid phase, atoms of the entire push-pull system of enaminoquinones lie practically in one plane.

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INTRODUCTION

Organic molecules with conjugated acceptor quinone fragment Q and donor amine function NR_2 can be designated by the general formula $Q–S_p–NR_2$, where S_p is an unsaturated bridging fragment. These compounds are promising for the use in nonlinear optical blocks [1-5], molecular electronic devices [6-8], and also systems modeling the work of natural photosynthetic centers [9-12].

The family of the $Q–S_p–NR_2$ structure type still contains insufficiently studied but interesting types of compounds. Enaminoquinones $Q_{Hal}–CH=CH–NR_2$ with a halogenated quinone fragment Q_{Hal}, which not only enhances the push-pull character of the $Q_{Hal}–CH=CH–NR_2$ system but also opens new ways to functionalize the quinone core, belong to them [13-15]. The aim of this work was the synthesis of 2-diethylaminovinyl-1,4-quinones $Q_{Hal}–CH=CH–NEt_2$ with different Q_{Hal} and the analysis of their structure and packing.

EXPERIMENTAL

Materials and methods. ^1H and ^{19}F NMR spectra were measured on a Bruker AV-300 spectrometer (^1H operating frequency 300.13 MHz, ^{19}F operating frequency 282.36 MHz); $CDCl_3$ (H 7.24 ppm) and C_6F_6 (F 162.9 ppm with respect to $CFCl_3$) were used as the internal standards. Melting points were determined on a Mettler Toledo apparatus with a FP 900 Thermosystem cell and were not corrected. The C, H, N elemental analysis was conducted on a Carlo Erba Model 1106,

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F instrument by spectrophotometry. Accurate masses of molecular ions were determined on a high-resolution Thermo Scientific DFS mass spectrometer (Double Focusing Sector Mass Spectrometer, DFS High Resolution GC/MS). IR spectra were measured on a Vector-22 instrument from the samples pressed in pellets with KBr. UV spectra were recorded on a Cary5000 apparatus in methylene chloride. The reaction course and the purity of products were controlled by thin-layer chromatography (TLC) on Merck Silica gel 60 F254c plates. Silica gel (50-160 mesh) was applied for chromatography. Amines Et_2NH, Et_3N, as well as solvents were distilled before the use. Acetaldehyde was used without preliminary purification.

Synthesis of (*E*)-2-(2-(diethylamino)vinyl)-3,5,6,7,8-pentafluoronaphthalene-1,4-dione (8). To a solution of quinone **5** (0.050 g, 0.188 mmol) in CH_2Cl_2 (2.0 mL) a solution of Et_2NH (0.014 g, 0.188 mmol) and MeCHO (0.026 g, 0.590 mmol) in CH_2Cl_2 (2.0 mL) was added. The reaction mixture was stirred for 1 h at room temperature and then evaporated at lowered pressure. The residue was purified by TLC (silica gel Merck on a glass plate, 1:2 Et_2O–hexane) and 0.021 g (32%) of quinone **8** as blue crystals and 0.020 g (34%) of quinone **9** [16] as red oil were obtained.

8: m.p. 189.7 °C (with decomposition). UV (CH_2Cl_2) λ_{max}, nm (lgε): 599 (4.07), 331 (4.40). ^{19}F NMR ($CDCl_3$, δ, ppm, *J*, Hz): 30.93 (br. s., 1F, F^3), 22.60 (m., 2F, $F^{5,8}$), 16.70 (m., 1F, F^6 or F^7), 14.24 (m., 1F, F^6 or F^7). ^1H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 7.90 (d.d., 1H, CH, $^3J_{HH} = 13.4$, $J = 2.6$), 5.24 (d., 1H, CH, $^3J_{HH} = 13.4$), 3.35 (q., 4H, $2CH_2$, $^3J_{HH} = 7.1$), 1.24 (t., 6H, $2CH_3$, $^3J_{HH} = 7.1$). IR, cm^{-1}: 2987, 2962, 2945, 2879, 1678, 1649, 1614, 1585, 1547, 1502, 1470, 1454, 1435, 1381, 1365, 1340, 1313, 1250, 1184, 1147, 1126, 1095, 1078, 1051, 1018, 987, 966, 953, 933, 841, 822, 802, 787, 764, 611, 550. Found $[M]^+$ 345.0780. Calculated $[M]^+$ for $C_{16}H_{12}F_5NO_2$ 345.0783. Found (%): C 55.55, H 3.78, N 3.65. Calculated for $C_{16}H_{12}F_5NO_2$ (%): C 55.66, H 3.50, N 4.06.

The synthesis of 2,3,5-tribromo-6-(2′-(diethylamino)vinyl)-benzo-1,4-quinone (**2b**, 18%) [17] from bromanil and 2-diethylaminovinyl-3-bromo-1,4-narhthoquinone (**4b**, 35%) from 2,3-dibromo-1,4-naphthoquinone **6** was performed by the similar procedure. In 1 h, a reaction of 2-methoxypentafluoro-1,4-naphtnoquinone resulted in a mixture of initial quinone and unidentified products.

The single crystal X-ray diffraction (XRD) study of compounds **2b**, **4b**, and **8** was conducted on an automated Bruker KAPPA APEX II CCD diffractometer: graphite monochromator; $\lambda MoK_\alpha = 0.71073$ Å; ω–φ scanning; temperature 296 K. Absorption correction was applied semi-empirically using the SADABS program [18]. The structures were solved by a direct method using the SHELXT-2014/5 program [19] and refined first in the isotropic and then anisotropic approximations using the SHELXL-2014/7 program [19]. Hydrogen atoms in the structures were placed in geometrically calculated positions and refined by the riding model. The main parameters of the single crystal XRD experiment are listed in Table 1. The figures were drawn and the analysis of intermolecular interactions was carried out using the PLATON [20] and MERCURY [21] programs, respectively.

Full tables of interatomic distances and bond angles, atomic coordinates and displacement parameters have been deposited with the Cambridge Crystallography Data Center (CCDC 1971279, 1971280, 1971281 for **2b**, **4b**, **8** respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

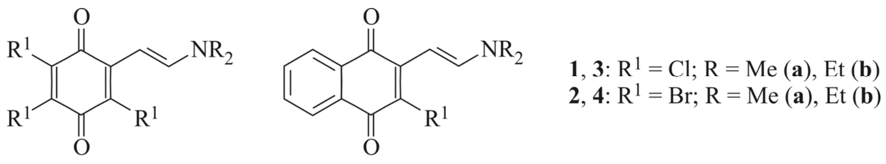
It has been previously shown that 2-diethylaminovinyl-1,4-quinones **1b**, **2b** formed with a low yield (NMR yield ~70% and ~60%, product yield ~50% and ~40% for **1b** and **2b** respectively) in the interaction of Et_3N with tetrachloro- and tetrabromo-1,4-benzoquinones in benzene [15]. The interaction of 2,3-dibromonaphtho-1,4-quinone with Et_3N in CH_2Cl_2 by the above described procedure yielded 2-diethylaminovinyl-1,4-quinone **4b** only in trace amounts [22]. A low yield of quinones **1b**, **2b**, and **4b** is due to two factors: firstly, a part of initial quinones was consumed to oxidize Et_3N to enamine in the reaction; secondly, the lability of formed enaminoquinones that partially decomposed during isolation processes.

A more efficient method for preparing 2-dialkylaminovinyl-1,4-quinones was described by Henbest and coworkers. It consisted in the interaction of halogenated *para*-quinone with an equivalent amount of acetic or crotonic aldehyde and two

TABLE 1. Crystallographic Data and Details of the Single Crystal XRD Experiment

Parameter	**2b**	**4b**	**8**
Chemical formula	$C_{12}H_{12}Br_3NO_2$	$C_{16}H_{16}BrNO_2$	$C_{16}H_{12}F_5NO_2$
Formula weight	441.96	334.21	345.27
Crystal system	Triclinic	Monoclinic	Triclinic
Space group; Z	P-1; 2	$P2_1/c$; 4	P-1; 2
Unit cell parameters: a, b, c, Å;	7.3381(3), 10.6657(4), 10.6823(4);	7.9468(4), 18.2894(8), 10.4268(4);	8.1031(12), 9.8177(13), 9.8306(13);
α, β, γ, deg	62.980(2), 70.854(2), 84.943(2)	90, 105.243(2), 90	106.744(6), 103.086(6), 97.146(6)
V, Å^3	701.76(5)	1462.1(1)	714.2(2)
d_{calc}, g/cm^3	2.092	1.518	1.605
μ, mm^{-1}	8.615	2.812	0.149
θ range, deg	2.15-30.04	2.23-27.60	2.21-25.78
Reflections measured / unique (R_{int})	14287 / 3724 (0.0512)	22872 / 3379 (0.0517)	11774 / 2715 (0.0641)
Observed reflections with $I > 2\sigma(I)$	3075	2349	1410
R_1, wR_2 over $I > 2\sigma(I)$	0.0435, 0.0988	0.0584, 0.1553	0.0541, 0.0968
R_1, wR_2 over unique reflections	0.0553, 0.1062	0.0902, 0.1859	0.1295, 0.1191
GOOF	1.009	1.043	1.023
CCDC	1971279	1971280	1971281

equivalents of Alk_2NH in a benzene or water-dioxane solution. Both enaminoquinones and products of the dialkylamino group substitution for the halogen atom formed here [23]. In order to avoid the formation of the latter, Fokin and coauthors [24] proposed a modified procedure, according to which, an aqueous dialkylamine solution (R_2NH, R = Me, Et) was gradually added to a solution of 1,4-quinone and aldehyde in aqueous dioxane at pH 6-7. Under these conditions, respective enaminoquinones **1a** and **3a** were obtained with a yield of 70-86% [24] (Scheme 1). Later it was shown that the use of the inverse order of adding the reagents, namely, the addition of the amine and aldehyde solution to the solution of 1,4-quinone in toluene also resulted in target 2-dialkylaminovinyl-1,4-quinones **1a, b**, **2b**, and **3b** with high yields (67-90%) [17] (Scheme 1).



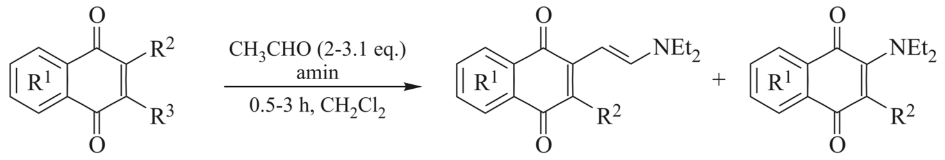
1a,b
2a,b

3a,b
4a,b

1, **3**: R^1 = Cl; R = Me (**a**), Et (**b**)
2, **4**: R^1 = Br; R = Me (**a**), Et (**b**)

Scheme 1.

Having analyzed the available methods for obtaining enaminoquinones, we selected the variant with the inverse order of mixing reagents and used it, including for the preparation of previously unknown polyfluorinated enaminoquinone **8**. Under the optimized conditions (EXPERIMENTAL), namely, by the interaction of hexafluoro-1,4-naphthoquinone **5** with a solution of Et_2NH (1 eq.) and MeCHO (3.1 eq.) in CH_2Cl_2, we managed to obtain enaminoquinone **8** with a yield of 32% (Scheme 2). Here, along with **8** as a by-product naphthoquinone **9** formed (34%). Under similar conditions, 2,3-dibromo-1,4-naphthoquinone **6** gave 2-diethylaminovinyl-3-bromo-1,4-naphthoquinone **4b** with a 35% yield.



5: R^{1,2,3} = F; Et$_2$NH (1 eq.) **8**, 32% **9**, 34%
6: R^1 = H; R^{2,3} = Br; HNEt$_2$ (1 eq.) **4b**, 35%
7: R^1 = H; R^2 = Br; R^3 = OMe; HNEt$_2$ (1 eq.) **4b**, 8%

Scheme 2.

Crystals of compounds **2b** and **4b** were grown from a dichlorometane–heptane (1:1) mixture at –5 °C for 30 and 7 days respectively. Crystals of compound **8** were grown for 7 weeks in a closed bottle from benzene by gas exchange with hexane at room temperature.

According to the single crystal XRD data, the tribromobenzoquinone fragment in **2b** as well as 2-bromo-1,4-naphthoquinone fragment in **4b** and pentafluoro-1,4-naphthoquinone one in **8** are almost planar. The mean average square deviation from the plane drawn through all non-hydrogen atoms of these fragments is 0.070 Å, 0.032 Å, and 0.036 Å for **2b**, **4b**, and **8** respectively. In all three compounds, the aminovinyl fragment is also planar and lies in the same plane as the tribromobenzoquinone fragment in **2b**, the 2-bromo-1,4-naphthoquinone fragment in **4b**, and pentafluoro-1,4-naphthoquinone one in **8**. In the molecules of compounds **2b** and **8**, ethyl groups are directed in different sides from the plane in which the other atoms lie, whereas in the **4b** molecule, ethyl groups are located at one side of the plane in which the other atoms lie. Fig. 1 depicts the molecular structures of **2b**, **4b**, **8** molecules; their geometric parameters correspond to average statistical values in the 3σ limit [25]. Intermolecular interactions were analyzed using the PLATON [20] and MERCURY [21] programs.

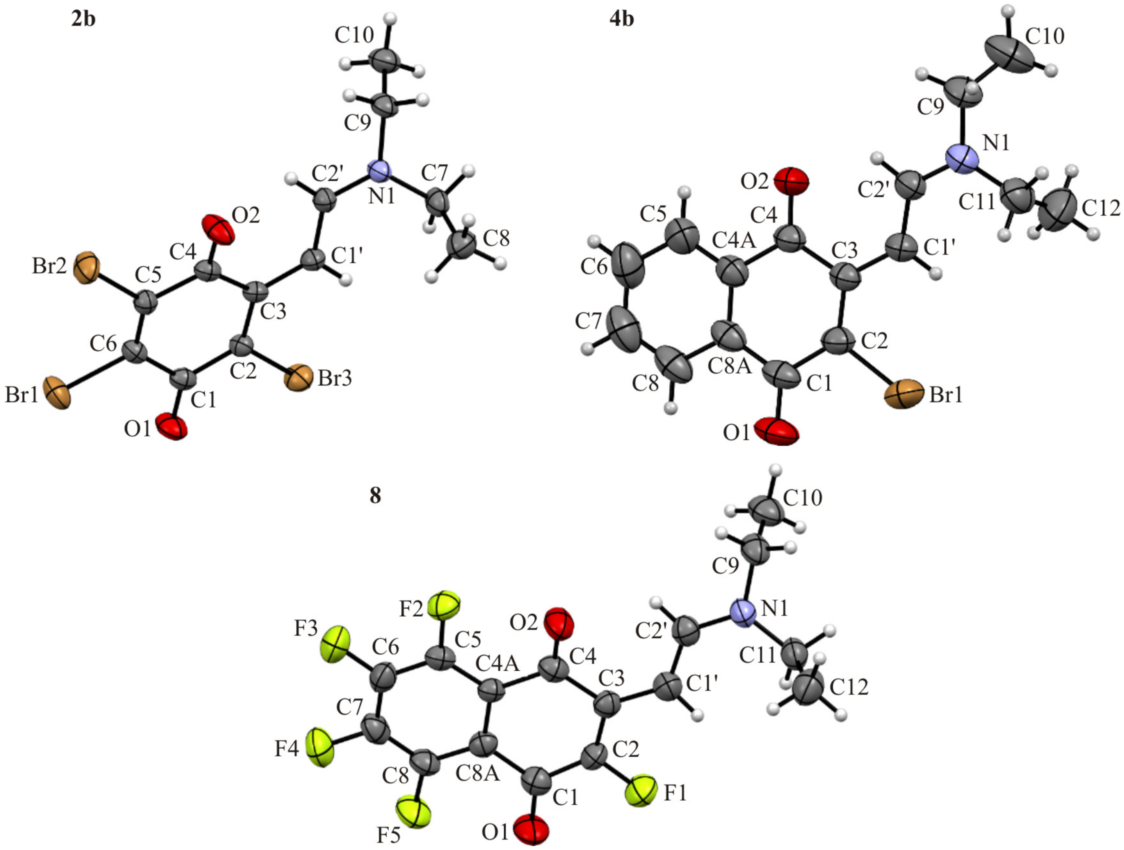


Fig. 1. Molecular structures of enaminoquinones **2b**, **4b**, and **8**.

The conjugated molecules having a planar structure are characterized by the stacked packing, including π-stacking interactions [26]. The occurrence of substituents often leads to significant lateral displacements of the neighboring molecules in the stacks. Just this situation is also observed for the crystal packing of compound **2b** (Fig. 2) where the molecules are packed with the formation of a staircase structure instead of stacks. The distance between the centroids of the neighboring molecules in the stack is 3.965(2) Å, and O…π and Br…π interactions are observed instead of π-stacking interactions (O1 and Br3 atoms interact with the π-system of the benzoquinone fragment of the neighboring chains). The distance from the O1 atom to the centroid (Cg) is 3.504(4) Å and the distance from the Br3 atom to Cg is 3.922(2) Å. There are weak C9–H…O1 hydrogen bonds between the neighboring stacks-staircases along the *c* axis (Fig. 2); parameters of these bonds are given in Table 2. A polychlorinated analog of compound **2b** was found in CCDC [27] whose crystal packing is similar to that of **2b** because of the presence of stacks with a large lateral displacement, inside which there are O…π and Cl…π interactions.

The crystal structure of compound **4b** has the stacking character (head-to-tail) due to π-stacking interactions between the π-systems of naphthoquinone fragments with the Cg…Cg distance of 3.737(2) Å and the interplanar distance of 3.49 Å, which is supplemented by the O…π interaction with the O1 atom…centroid (Cg) distance of 3.692(5) Å (Fig. 3). The neighboring stacks are packed in tiles and linked with each other by weak C7–H…O1 and C9–H…O1 hydrogen bonds (Table 2). In CCDC there is a close analog of compound **4b** which is distinct in that it contains a quinoline-5,6-dione fragment instead of the naphthoquinone one [28]. Despite that the crystals of compounds with naphthoquinone and quinoline-5,6-dione fragments are practically isostructural, a substantially larger lateral displacement is observed in the heterocyclic derivative (the minimum distance between the centroids of the neighboring molecules is 4.490 Å).

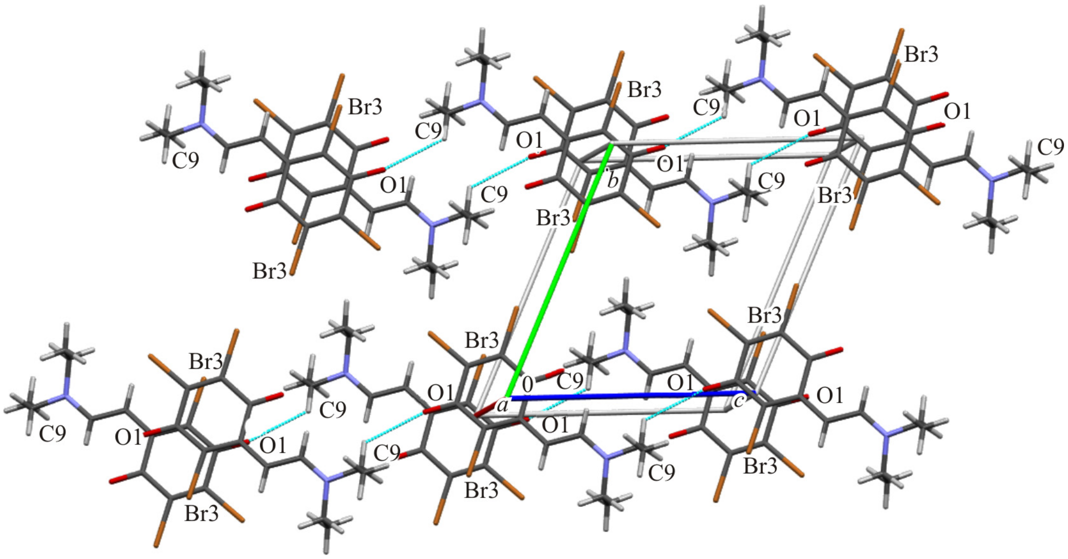


Fig. 2. Fragment of the crystal structure of enaminoquinone **2b**.

TABLE 2. Parameters of Hydrogen Bonds in Compounds **2b** and **4b**

Compound	Interaction	Parameter		
		H…O, Å	C…O, Å	C–H…O, deg
2b	C9–H9a···O1	2.59	3.207(7)	121
4b	C7–H7···O1	2.47	3.278(7)	145
	C9–H9b···O1	2.59	3.508(8)	157

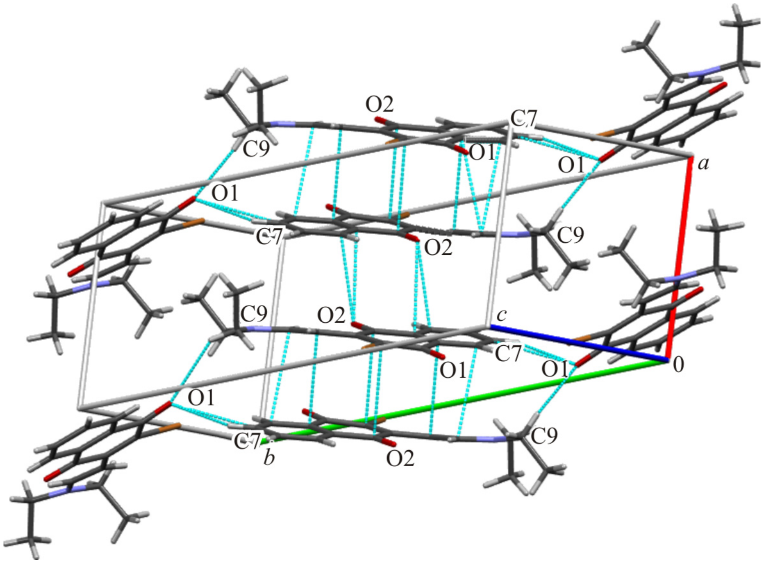


Fig. 3. Fragment of the crystal structure of enaminoquinone **4b**.

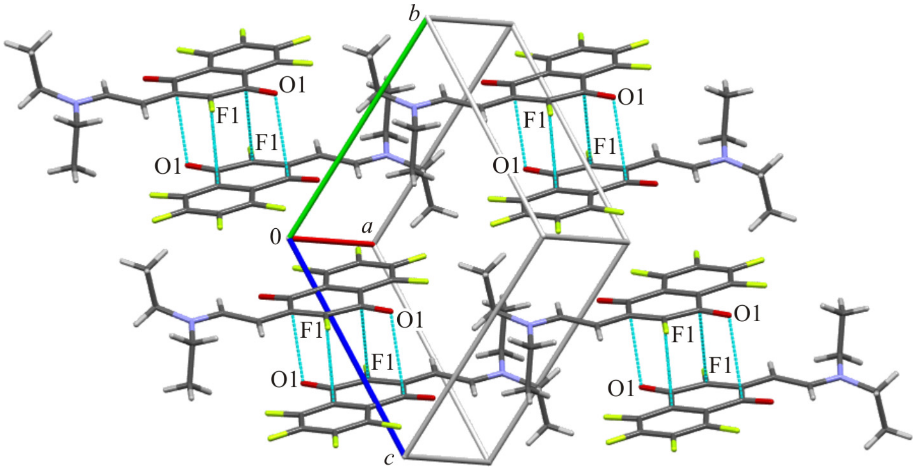


Fig. 4. Fragment of the crystal structure of polyfluorinated quinone **8**.

The crystal packing of compound **8** is characterized by the presence of the π-stacking interaction between π systems of naphthoquinone fragments with the Cg…Cg distance of 3.634(2) Å and the interplanar distance of 3.27 Å. The F…π and O…π interactions with the F1…centroid (Cg) distance of 3.334(2) Å [29] and the O1…centroid (Cg) distance of 3.399(2) Å are also observed in these stacks (Fig. 4). Unlike **2b** and **4b**, in the crystal structure of **8**, hydrogen bonds are absent.

CONCLUSIONS

Thus, in this work, diethylaminovinyl derivatives of halogenated 1,4-quinones were synthesized. It is shown that the reaction of polyfluorinated 1,4-naphthoquinones with in situ obtained *N*,*N*-diethyl-*N*-vinylamine gives a product with enamine substitution for the fluorine atom in the quinone ring. Molecular and crystal structures of diethylaminovinyl derivatives of halogenated 1,4-quinones are solved. The obtained data can be used to deduce correlations between the structure and optical characteristics of Q_{Hal}–CH=CH–NR_2 systems.

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CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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