Research Article

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To what extent can a conjugation between two pairs of *peri*-nitro and *peri*-amino groups be realized through the naphthalene core?

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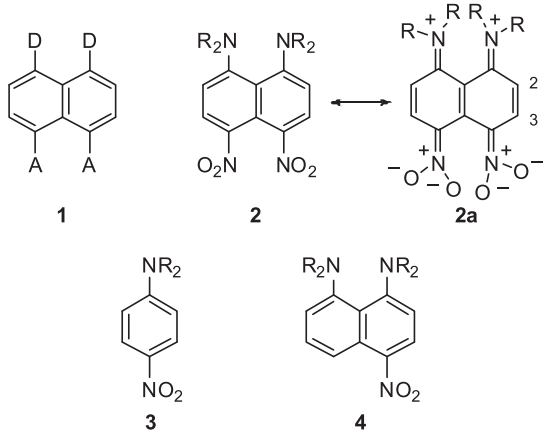
Through-conjugation for a wide range of 1,8-diamino-4,5-dinitronaphthalenes (*N*-acylated, *N*-alkylated, *N,N′*-bridged, *N*-heterocyclic, and *N*-deprotonated compounds) was for the first time quantified in solution by means of ultraviolet–visible and proton nuclear magnetic resonance spectroscopy and compared with that of the simpler naphthalene and benzene push-pull systems. Surprisingly, an extent of conjugation in 1,8-diamino-4-nitro- and 1,8-diamino-4,5-dinitronaphthalenes measured in dimethyl sulfoxide is commensurable. On the whole, the repulsive *peri*-interactions between the amino groups in systems with *N*-alkylated and *N*-deprotonated amino groups are more favorable for an effective D-π-A charge transfer than in *N,N′*-bridged compounds (perimidines, 2,3-dihydroperimidines and perimidin-2-ones). The best electron donors from *peri*-positions are pyrrolidin-1-yl and methylamido groups. The conclusions obtained from solution studies were deepened by solid- state X-ray experiments for a number of push–pull naphthalenes, including 6,7-dinitroperimidine *N*-anion and two representatives of 4,5-diaminonaphthalene-1,8-dicarbaldehydes. In particular, they helped to trace changes in the bond order redistribution and twisting of the naphthalene core. The latter reaches a record value of 27° for 4,5-dinitro-1,8-di(pyrrolidin-1-yl)naphthalene. Copyright © 2013 John Wiley & Sons, Ltd.

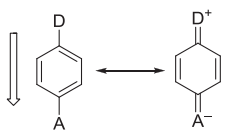
Keywords: 1,8-diamino-4,5-dinitronaphthalenes; 4,5-diaminonaphthalene-1,8-dicarbaldehydes; arylamide anions; *peri*-interaction; push–pull donor–acceptor system

INTRODUCTION

Organic molecules of D-π-A type with π-donor and π-acceptor substituents on the opposite ends of the conjugated chain are extensively studied compounds because of their nonlinear optical[1–3] and some other[2,4,5] interesting properties including application as molecular sensors.[6] For example, interaction between +*M* (D) and −*M* (A) substituents, called a through-conjugation, is known to exist in *para*-disubstituted benzenes.[7,8] The true structure of such push–pull molecules is a linear combination of the neutral aromatic and localized zwitterionic forms (Scheme 1).[7,9] Depending on the donor–acceptor strength of groups A and D, the contribution of the quinoid resonance structure may be significant, but, owing to high benzene ring aromaticity, it is always counterbalanced with the benzenoid structure so that the intramolecular charge transfer is never complete.[9,10]

Because aromaticity of naphthalene is markedly lower than that of benzene,[11] push–pull naphthalene systems are rather attractive, and some of them were in a focus of recent investigations devoted to intramolecular charge transfer processes,[12] designing new fluorophores,[13,14] π-extended structures,[15] and colorimetric indicators.[16] Many of the explored systems are 1,4-di-, 1,5-di-, or 1,4,5-trisubstituted naphthalenes, and much less is known about their 1,4,5,8-tetrasubstituted analogs **1**.[17,18] Meanwhile, in such derivatives with the doubled fragment of the benzene type, the efficiency of through-conjugation and the degree of electron transfer via the aromatic π-system may be higher, in particular because of a possibility of resonance interaction between D and A groups at positions 1,5 and 4,8, which is impossible in the benzene series.





Scheme 1. Direction of through-conjugation in *para*-D-π-A benzenes

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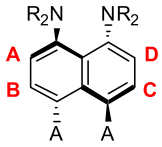
In the present work, we have synthesized and for the first time studied the possible limits of the through-conjugation in a number of 1,8-diamino-4,5-dinitronaphthalenes **2** and closely related molecules **3** and **4**. A set of solid reasons was put behind this choice (A = NO_2, D = NR_2): (i) The difference between the Hammett σ_p constants for these groups is high;[19] (ii) The nitro-aromatics are an extremely important class of compounds with varied applications, and nitro-amino push–pull systems are frequently in the center of theoretical[9,20] and experimental[9,15] investigations; and (iii) Easy and wider changes in the degree of resonance interaction are achievable; thus, in addition to common ways of the amino group modification, a possibility for internitrogen bridging appears. Noteworthy is that effective conjugation of the amino and nitro groups in systems such as **2** is usually accompanied by molecular distortion caused by bulkiness of the adjacent *peri*-substituents and their electrostatic repulsion (see bipolar structure **2a**). Although the degree and the mode of this distortion are often unpredictable,[18,21] most of them are reduced to a strong twisting of the naphthalene core, expressed via a torsion angle ABCD in structure **5** (up to 23–26°[18]). Consequently, we also resolved the X-ray structures of nine new molecules of this and related types.



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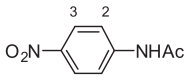
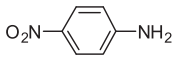
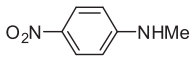
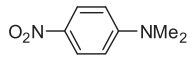
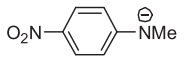
The spin–spin coupling constants $^3J_{2,3}$ (structure **2a**, proton nuclear magnetic resonance [^{1}H NMR] spectroscopy) and the position of the long-wave absorption band (λ_{max}, ultraviolet–visible [UV–Vis] spectroscopy) were chosen as the criteria of π-conjugation and intramolecular charge transfer. These parameters are known to be sensitive to the double bond localization [C(2)–C(3) aromatic bond], which will increase on going from **2** to **2a**.[20,22] Finally, dimethyl sulfoxide (DMSO) was used as the solvent in all measurements because of the solubility demands and the ability of this solvent to solubilize ionic species (*N*-anions) and stabilize zwitterionic forms of type **2a**.

Table 1. Proton NMR and UV–Vis data for *p*-nitroanilines **6–10**

Compound	^{1}H NMR (DMSO-d_6)				λ_{max} (lgε) (nm) (DMSO)
	H-3	H-2	Δδ [a]	$^3J_{2,3}$	
 **6**	8.21	7.82	0.39	8.95	332 (4.11)
 **7**	7.95	6.60	1.35	9.16	389 (4.05)
 **8**	8.01	6.60	1.41	9.47	400 (4.23)
 **9**	8.05	6.76	1.29	9.48	408 (4.33)
 **10**	7.41	5.97	1.44	9.95	484 (4.40)

NMR, nuclear magnetic resonance; UV–Vis, ultraviolet–visible; DMSO, dimethyl sulfoxide.
[a] $\Delta\delta = \delta$(H-3) − δ(H-2).

EXPERIMENTAL

General

The ^{1}H NMR spectra were recorded on a Bruker (Rostov-on-Don, Russian Federation) DPX-250 (250 MHz) spectrometer with the solvent as the internal standard (δ/ppm, ^nJ/Hz). UV–Vis spectra were obtained in DMSO on a Varian Cary-50 Probe (Rostov-on-Don, Russian Federation) spectrometer. Thin layer chromatography was carried out on Al_2O_3 with Brockmann activity III and on silica gel (70–230 mesh, MERCK, Germany). The progress of reactions and the purity of products were monitored by thin layer chromatography on Al_2O_3 and Silufol plates using the development with iodine vapor. The melting points were measured in sealed capillaries and are uncorrected. The solvents were purified and dried by standard methods.

Preparation of starting materials

The compounds used in this work are listed in Tables 1–3.

Common *p*-nitroanilines **6**, **7**, **9** were recrystallized from EtOH. *N*-Methyl-*p*-nitroaniline **8** was synthesized from $MeNH_2$·HCl and *p*-nitrochlorobenzene in refluxing pyridine, as described in the literature (this method may be also applied for the synthesis of *N*,*N*-dimethyl derivative **9**; *p*-nitrochlorobenzene may be substituted by its bromo analog).[23] Anion **10** was generated through the addition of a powdered KOH (3–5 molar excess) to the corresponding solutions; spectral readings were performed in regular (0.5–2 h) intervals to ensure the ionization is complete.

Model α-nitronaphthalenes and related compounds **11** (dark blue-violet crystals with mp = 258–259 °C from MeCN),[24] **12**,[25] **13**,[26] and **14**[27] were prepared in accord with the previously published procedures.

Nitronaphthalenes **15** and **24** were obtained by nitration (1.6 equiv HNO_3 in concentrated [conc.] H_2SO_4, −30 °C, 10 min) of 1,8-di(pyrrolidin-1-yl) naphthalene[28] following the procedure described for the nitration of 1,8-bis(dimethylamino)naphthalene.[27] The compounds were separated by chromatography on Al_2O_3 with CH_2Cl_2 elution, which gave first **15** (main purple fraction) followed by **24** (red fraction).

*4-Nitro-1,8-di(pyrrolidin-1-yl)naphthalene (**15**)*

Yield 19%, dark maroon leaflets with mp = 170–171 °C (EtOAc). Found: C, 69.27; H, 6.88; N, 13.42%. Calcd for $C_{18}H_{21}N_3O_2$: C, 69.43; H, 6.80; N, 13.49%. ^{1}H NMR ($CDCl_3$): 1.90 (m, 8H), 3.13 (m, 4H), 3.28 (m, 2H), 3.54 (m, 2H), 6.33 (d, 1H, H-2, ^3J = 9.47 Hz), 6.63 (dd, 1H, H-7, ^3J = 7.90 Hz, ^4J = 0.95 Hz), 7.42 (dd, 1H, H-6, ^3J = 7.90 Hz, ^3J = 8.53 Hz), 8.41 (m, 2H, H-3,5). Perchlorate **15**·$HClO_4$: beige crystals with mp = 180–182 °C (decompose [decomp.], MeCN). ^{1}H NMR (CD_3CN): 2.18 (m, 4H), 2.35 (m, 4H), 3.42 (m, 4H), 3.82 (m, 4H), 7.95 (m, 2H, H-2,6), 8.04 (dd, 1H, H-7, ^3J = 7.74 Hz, ^4J = 1.11 Hz), 8.32 (d, 1H, H-3, ^3J = 8.48 Hz), 8.44 (dd, 1H, H-5, ^3J = 8.85 Hz, ^3J = 1.11 Hz), 19.22 (br s, 1H, NH).

*4,5-Dinitro-1,8-di(pyrrolidin-1-yl)naphthalene (**24**)*

Yield 3%, red crystals sparingly soluble in EtOAc, $CHCl_3$, MeCN, EtOH, acetone, toluene, or DMSO, good solubility in CH_2Cl_2. The compound turns

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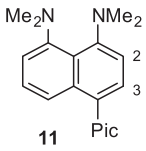
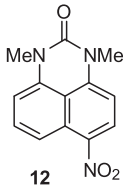
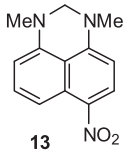
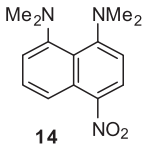
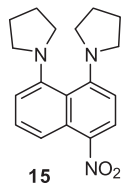
Table 2. Proton NMR and UV–Vis data for α-picryl-**11** and α-nitronaphthalenes **12–15**

Compound	^{1}H NMR (DMSO-d_6)				λ_{max} (lgε) (nm) (DMSO)
	H-3	H-2	$\Delta\delta^a$	$^3J_{2,3}$	
 **11**	7.21	6.95	0.26	8.30	350 (4.13)
 **12**	8.40	6.76	1.64	9.00	450 (3.75)
 **13**	8.40	6.54	1.86	9.08	465 (4.15)
 **14**	8.26	6.82	1.44	9.16	484 (4.19)
 **15**	8.25	6.50	1.75	9.59	530 (4.28)

NMR, nuclear magnetic resonance; UV–Vis, ultraviolet–visible; DMSO, dimethyl sulfoxide.

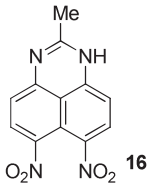
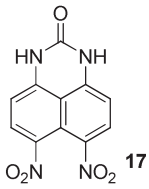
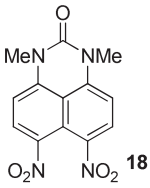
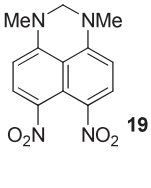
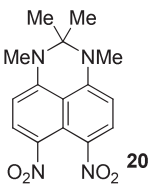
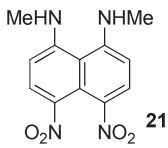
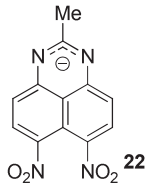
dark above 290 °C, but no melting is observed up to 360 °C. Found: C, 60.39; H, 5.28; N, 15.33%. Calcd for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66; N, 15.72%. ^{1}H NMR ($CDCl_3$): 1.98 (m, 4H), 2.24 (m, 4H), 2.71 (m, 2H), 3.16 (m, 2H), 3.37 (m, 2H), 3.55 (m, 2H), 6.44 (d, 2H, H-2,7, ^3J = 9.12 Hz), 8.16 (d, 2H, H-3,6, ^3J = 9.12 Hz). ^{1}H NMR (DMSO-d_6): 1.59 (m, 2H), 1.91 (m, 2H), 2.00 (m, 2H), 2.11 (m, 2H), 2.54 (m, 2H), 3.06 (m, 2H), 3.40 (m, 2H), 3.70 (m, 2H), 6.64 (d, 2H, H-2,7, ^3J = 9.28 Hz), 8.10 (d, 2H, H-3,6, ^3J = 9.28 Hz).

Several dinitronaphthalenes were prepared in accord with the published data: **16**,[29] **18**,[26] and **23**.[30] Syntheses of other symmetrical *peri*-disubstituted derivatives and their properties are as follows.

*6,7-Dinitro-1H-perimidine-2-one (**17**) and 4,9-dinitro-1H-perimidine-2-one (**17-ortho**)*

To a suspension of 1*H*-perimidine-2-one (1.84 g, 10 mmol) in glacial AcOH (75 mL), a solution of conc. HNO_3 (d = 1.5, 1.05 mL, 25 mmol) in AcOH (25 mL) was added dropwise at 5–10 °C for 15 min with stirring. After

Table 3. Proton NMR and UV–Vis data for dinitronaphthalenes **16–27** and dialdehydes **28** and **29**

Compound	^{1}H NMR (DMSO-d_6)			λ_{max} (lgε) (nm) (DMSO)
	H-3	H-2	$^3J_{2,3}$	
 **16**	8.33	6.97	8.77	439 (4.00)
 **17**	8.34	6.88	8.85	420 (4.09)
 **18**	8.49	7.17	9.00	414 (4.18)
 **19**	8.25	6.70	9.06	439 (4.23)
 **20**	8.25	6.77	9.10	446 (3.25)
 **21**	8.18	6.63	9.10	448 (4.06)
 **22**	8.17	6.76	9.12	557 (3.76)

(*Continues*)

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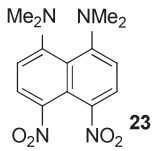
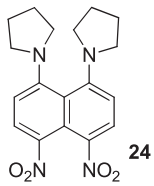
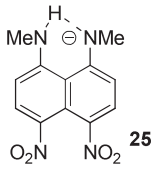
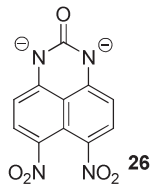
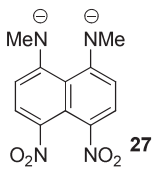
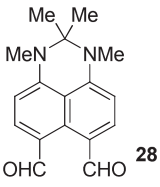
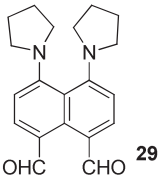
Table 3. *(Continued)*

Compound	^{1}H NMR (DMSO-d_6)			λ_{max} (lgε) (nm) (DMSO)
	H-3	H-2	$^3J_{2,3}$	
 **23**	8.11	6.85	9.19	476 (3.75)
 **24**	8.10	6.64	9.28	494 (4.15)
 **25**	7.98	6.38	9.30	520 sh. (3.62)
 **26**	7.93	6.36	9.32	568 (3.96)
 **27**	7.78	6.14	9.77	598 sh. (3.48)
 **28**	7.99	6.79	8.59	424 (3.62)
 **29**	7.78	6.65	8.76	470 (4.24)

NMR, nuclear magnetic resonance; UV–Vis, ultraviolet–visible; DMSO, dimethyl sulfoxide.

Table 4. Selected X-ray geometrical characteristics [C(2)–C(3) and N(1)–C(1) bond lengths, torsion angles, φ, between acceptors and aromatic rings, molecular twisting, ∠ABCD, internitrogen distances N(1)...N(2)] for studied push–pull molecules and model compounds

Compound	$r_{C(2)-C(3)}$ (Å)[a]	$r_{N(1)-C(1)}$ (Å)[b]	φ (°)[c]	∠ABCD (°)	$r_{N(1)...N(2)}$ (Å)	CCDC ref. code
7	1.382	1.355	2	—	—	NANILI02
8	1.371	1.358	2	—	—	FUXNAN
9	1.375	1.358	3	—	—	DIMNAN01
11	1.386	1.386	65[d]	15	2.838	NUPJIR
14	1.366	1.371	23	15	2.859	ZOSKAT
15	1.371	1.348	6	16	3.001	[e]
16·DMF	1.393	1.386	36	6	2.357 (2.989)[f]	[e]
16·MeCN	1.382	1.383	39	4	2.348 (2.983)	[e]
17-*ortho*	1.406	1.376	6	1	2.320	[e]
22	1.368	1.369	22	13	2.392 (3.117)	[e]
23	1.380	1.367	28	23	2.917 (2.976)	SORYEE
24	1.379	1.352	32	27	3.079 (3.020)	[e]
28	1.374	1.364	13	4	2.387	[e]
29	1.377	1.356	12	24	3.033	[e]
35	1.407	—	43	6	(2.946)	DNTNAP01
36	1.405	—	39	6	(3.094)	[e]

DMF, dimethylformamide; CCDC, Cambridge Crystallographic Data Centre.
[a]Average values for two bonds in the case of molecules **2** and **3**.
[b]Average values for two bonds in the case of molecule **2**.
[c]Average values in the case of two acceptors.
[d]For picryl group.
[e]This work.
[f]Values in parentheses are for nitro nitrogens.

additional stirring for 1 h at 20 °C, the red-brown reaction mass was gradually mixed with water (400 mL), and the residue was filtered off, washed with water, and dried in air. The products were washed with hot toluene (150 mL) to leave *peri*-dinitro isomer **17**, which is sparingly soluble in common organic solvents. Recrystallization of the compound from AcOH gave **17** (43–60% in a set of runs) as orange-brown crystals not melted up to 360 °C (darken above 305 °C). Found: C, 48.05; H, 2.10; N, 20.41%. Calcd for $C_{11}H_6N_4O_5$: C, 48.19; H, 2.21; N, 20.43%.

The toluene extract was evaporated to dryness, and the residue was chromatographed on silica gel with EtOAc elution. The first mobile fraction gave *ortho*-dinitro isomer **17-*ortho*** (7–9% in a set of runs) as brown needles with mp above 260 °C (decomp., EtOAc). Found: C, 48.12; H, 2.07; N, 20.29%. Calcd for $C_{11}H_6N_4O_5$: C, 48.19; H, 2.21; N, 20.43%. ^{1}H NMR (DMSO-d_6): 7.57 (d, 2H, H-6,7, ^3J = 9.47 Hz), 8.35 (d, 2H, H-5,8, ^3J = 9.47 Hz), 10.98 (br s, 2H, NH).

*1,8-Di(methylamino)-4,5-dinitronaphthalene (**21**)*

This was prepared using the following modified procedure.[31] A yellow suspension of compound **18** (0.40 g, 1.3 mmol), KOH (7.4 g, 0.13 mol, 100 equiv), and methanol (360 mL) was refluxed for 48 h until a clear dark red solution is received. After that, the solvent was distilled off, the

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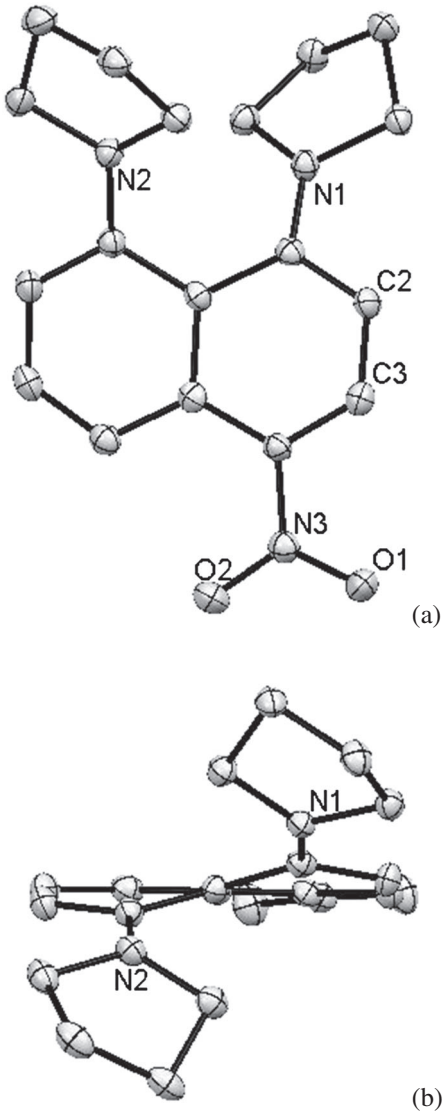

Figure 1. (a) Single-crystal X-ray structure of nitronaphthalene **15** (30% probability level, hydrogen atoms are omitted for clarity). (b) View along the naphthalene central bond showing out-of-plane bending of the two pyrrolidino groups

mixture was diluted with water (700 mL) and neutralized with conc. HCl to pH 3, and the precipitate thus formed was filtered off, washed with water, and then dried at room temperature. This gave dinitro derivative **21** (0.23 g, 64%) as small dark red crystals, melted at 263–264 °C (lit. mp = 235 °C.[31])

*1,3-Dimethyl-6,7-dinitro-2,3-dihydro-1H-perimidine (**19**)*

A mixture of compound **21** (0.05 g, 0.2 mmol), paraform (0.12 g, 4.0 mmol), methanol (25 mL), and several drops of conc. HCl (0.2 mL) was refluxed for 48–72 h until the starting compound is consumed (monitoring with Silufol–EtOAc). After that, the mixture was evaporated to dryness, and the residue was washed with water (10 mL) and then dried at room temperature. Chromatography (silica gel, acetone, first yellow fraction) gave compound **19** (0.01 g, 19%) as small brown-orange rhombs with mp = 263–265 °C (acetone). Found: C, 54.29; H, 4.17; N, 19.22%. Calcd for $C_{13}H_{12}N_4O_4$: C, 54.17; H, 4.20; N, 19.43%. ^{1}H NMR ($CDCl_3$): 3.13 (s, 6H, N–Me), 4.47 (s, 2H, NCH_2N), 6.49 (d, 2H, H-4,9, ^3J = 8.93 Hz), 8.23 (d, 2H, H-5,8, ^3J = 8.93 Hz).

*1,2,2,3-Tetramethyl-6,7-dinitro-2,3-dihydro-1H-perimidine (**20**)*

A mixture of compound **21** (0.05 g, 0.18 mmol), acetone (30 mL), and trifluoroacetic acid (0.05 mL) was refluxed for 10 h until the starting compound is consumed (monitoring with Al_2O_3–acetone). After that, the brown-red solution was evaporated to dryness in vacuum, and the residue was recrystallized from acetone. This gave compound **20** (0.03 g, 53%) as orange-brown crystals, darken above 280 °C (decomp. at 312 °C). Found: C, 57.08; H, 5.16; N, 17.59%. Calcd for $C_{15}H_{16}N_4O_4$: C, 56.96; H, 5.10; N, 17.71%. ^{1}H NMR ($CDCl_3$): 1.55 (s, 6H, C–Me), 3.10 (s, 6H, N–Me), 6.52 (d, 2H, H-4,9, ^3J = 8.94 Hz), 8.22 (d, 2H, H-5,8, ^3J = 8.94 Hz).

Dinitro compounds with the NH groups (**16**, **17**, and **17-*ortho***, in some extent **21**) are easily dissolved in aqueous Na_2CO_3 solutions with changing in color, which imply that these derivatives are relatively strong NH-acids.

Dialdehydes **28** and **29** were obtained by $POCl_3$/dimethylformamide (DMF) formylation of the corresponding *peri*-diamines.[32]

*1,2,2,3-Tetramethyl-2,3-dihydro-1H-perimidine-6,7-dicarbaldehyde (**28**)*

Temperature 0 to 20 °C, yield 33%. Dark yellow-brow crystals with mp = 190–191 °C (toluene). Other data see ref.[32]

*4,5-Di(pyrrolidin-1-yl)naphthalene-1,8-dicarbaldehyde (**29**)*

Temperature −5 to 0 °C, yield 12%. Dark yellow crystals with mp = 195–196 °C (decomp., toluene). Found: C, 74.27; H, 6.73; N, 8.54%. Calcd for

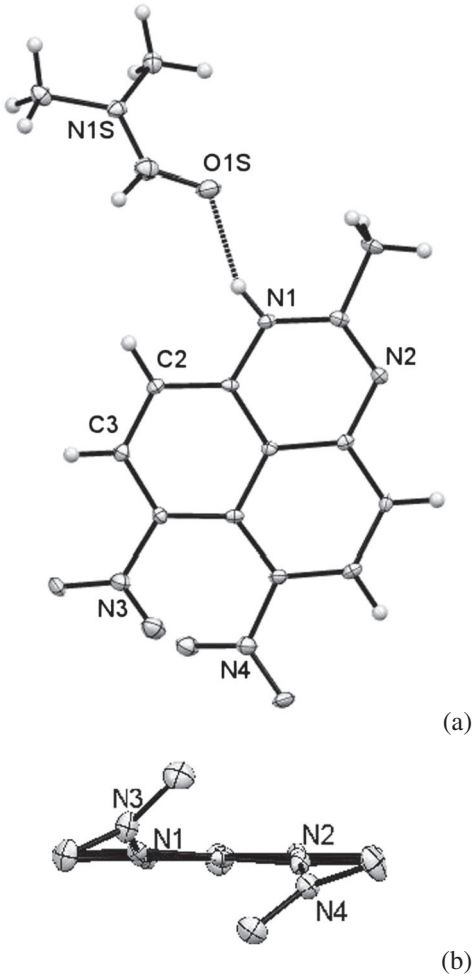

Figure 2. (a) Single-crystal X-ray structure of dinitroperimidine dimethylformamide (DMF) solvate **16**·DMF (30% probability level, intermolecular H-bonding with DMF molecule is shown). (b) View along the naphthalene central bond showing the twisting of the nitro groups

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$C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69%. ^{1}H NMR ($CDCl_3$): 1.60 (m, 2H), 1.94 (m, 4H), 2.19 (m, 2H), 2.69 (m, 2H), 3.18 (m, 2H), 3.39 (m, 2H), 3.56 (m, 2H), 6.53 (d, 2H, H-3,6, ^3J = 8.53 Hz), 7.92 (d, 2H, H-2,7, ^3J = 8.53 Hz), 9.78 (s, 2H, CHO).

*3,4-Dinitro-7,10-diphenyl-8,9-diazafluoranthene (**36**)*

A mixture of 5,6-dinitroacenaphthylene[33] (242 mg, 1 mmol), 3,6-diphenyltetrazine (240 mg, 1 mmol), and dry *o*-xylene (25 mL) was refluxed for 48 h. The solvent was removed, and the rest was chromatographed on Al_2O_3 with $CHCl_3$ elution. Evaporation of the main yellow fraction gave compound **36** (95 mg, 21%) as yellow-orange crystals with mp = 251–253 °C (decomp., benzene). Found: C, 70.03; H, 3.15; N, 12.34%. Calcd for $C_{26}H_{14}N_4O_4$: C, 69.95; H, 3.16; N, 12.55%. ^{1}H NMR ($CDCl_3$): 7.68 (m, 6H, Ph), 7.84 (d, 2H, H-1,6, ^3J = 7.72 Hz), 7.89 (m, 4H, Ph), 8.21 (d, 2H, H-2,5, ^3J = 7.72 Hz). UV–Vis ($CHCl_3$), λ_{max}/nm (lgε): 255 (4.58), 290 sh. (4.45), 420 (4.92).

X-ray crystallography

X-ray measurements were conducted with Bruker SMART (Moscow, Russian Federation) 1000 (for **15**, **17-*ortho***, and **29**; ω/2θ-scanning), Bruker APEX II (Moscow, Russian Federation) (for **16·DMF**, **16·MeCN**, **22**, **24**, and **28**; ω-scanning) and KM-4 Kuma Diffraction (Moscow, Russian Federation) (for **36**; ω/2θ-scanning) diffractometers (Mo-K_α line, graphite monochromator). Atomic coordinates, bond lengths, bond angles, and thermal parameters for all compounds have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ; fax: +44 1223 335 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers.

*Crystal data for **15***

(Obtained from MeCN): $C_{18}H_{21}N_3O_2$, M = 311.38, space group $P2_12_12_1$ (orthorhombic), a = 8.0937(12), b = 10.6030(16), c = 18.010(3) Å, V = 1545.6 (4) Å^3, Z = 4, D_c = 1.338 g cm^{-3}, μ(Mo-K_α) = 0.089 mm^{-1}, 120 K, 16 108 reflections collected, 3723 unique (R_{int} = 0.0731), 2440 reflections with $I > 2\sigma(I)$, 208 parameters, R_1 = 0.0513, wR_2 (all data) = 0.0997. CCDC reference number 911339.

*Crystal data for **16**·DMF*

(Obtained from DMF): $C_{15}H_{15}N_5O_5$, M = 345.32, space group Cc (monoclinic), a = 14.8622(18), b = 14.6665(17), c = 7.4433(9) Å, β = 110.373(2)°, V = 1521.0 (3) Å^3, Z = 4, D_c = 1.508 g cm^{-3}, μ(Mo-K_α) = 0.116 mm^{-1}, 100 K, 8217 reflections collected, 3566 unique (R_{int} = 0.0402), 3022 reflections with $I > 2\sigma(I)$, 229 parameters, R_1 = 0.0534, wR_2 (all data) = 0.1248. CCDC reference number 911340.

*Crystal data for **16**·MeCN*

(Obtained from MeCN): $C_{12}H_8N_4O_4$·MeCN, M = 313.28, space group Cc (monoclinic), a = 13.156(7), b = 14.790(7), c = 7.272(4) Å, β = 106.750(13)°, V = 1355.0(12) Å^3, Z = 2, D_c = 1.536 g cm^{-3}, μ(Mo-K_α) = 0.117 mm^{-1}, 100 K, 6870 reflections collected, 2949 unique (R_{int} = 0.0404), 2502 reflections with $I > 2\sigma(I)$, 210 parameters, R_1 = 0.0405, wR_2 (all data) = 0.0969. CCDC reference number 911341.

*Crystal data for **17-ortho***

(Obtained from DMF): $C_{11}H_6N_4O_5$, M = 274.20, space group $P\bar{1}$ (triclinic), a = 4.9626(6), b = 13.4805(16), c = 15.946(2) Å, α = 90.016(3)°, β = 95.406 (3)°, γ = 90.012(3)°, V = 1062.0(2) Å^3, Z = 4, D_c = 1.715 g cm^{-3}, μ(Mo-K_α) = 0.140 mm^{-1}, 295 K, 11262 reflections collected, 5355 unique (R_{int} = 0.0327), 2974 reflections with $I > 2\sigma(I)$, 361 parameters, R_1 = 0.0490, wR_2 (all data) = 0.1087. CCDC reference number 911342. There are two independent molecules in the unit cell.

*Crystal data for **22** [**16**·[1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene] proton transfer complex]*

(Obtained at −20 °C as trihydrate by slow diffusion of Et_2O into CH_2Cl_2 solution of the equimolar amounts of **16** and 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene;[34] brownish purple needles with mp = 114–116 °C (decomp.)): $C_{28}H_{36}N_6O_9$ [$C_{12}H_7N_4O_4$·$C_{16}H_{23}N_2O_2$·3H_2O], M = 600.63, space group $P2_1/c$ (monoclinic), a = 10.5916(14), b = 19.828(3), c = 14.1938 (18) Å, β = 101.221(3)°, V = 2923.9(7) Å^3, Z = 4, D_c = 1.364 g cm^{-3}, μ(Mo-K_α) = 0.103 mm^{-1}, 100 K, 32 607 reflections collected, 7056 unique (R_{int} = 0.1662), 3305 reflections with $I > 2\sigma(I)$, 395 parameters, R_1 = 0.0625, wR_2 (all data) = 0.1070. CCDC reference number 911343.

*Crystal data for **24***

(Obtained from CH_2Cl_2): $C_{18}H_{20}N_4O_4$, M = 356.38, space group $C2/c$ (monoclinic), a = 13.0257(13), b = 9.7142(13), c = 13.0509(15) Å, β = 103.001 (3)°, V = 1609.1(3) Å^3, Z = 4, D_c = 1.471 g cm^{-3}, μ(Mo-K_α) = 0.106 mm^{-1}, 100 K, 8230 reflections collected, 2343 unique (R_{int} = 0.0457), 1696 reflections with $I > 2\sigma(I)$, 119 parameters, R_1 = 0.0445, wR_2 (all data) = 0.1022. CCDC reference number 911344.

*Crystal data for **28***

(Obtained from CH_2Cl_2): $C_{17}H_{18}N_2O_2$, M = 282.33, space group $Pna2_1$ (orthorhombic), a = 20.036(2), b = 24.036(3), c = 11.4021(12) Å, V = 5490.9 (10) Å^3, Z = 16, D_c = 1.366 g cm^{-3}, μ(Mo-K_α) = 0.091 mm^{-1}, 100 K, 44 350 reflections collected, 10 231 unique (R_{int} = 0.0821), 6579 reflections with $I > 2\sigma(I)$, 817 parameters, R_1 = 0.0708, wR_2 (all data) = 0.1572. CCDC reference number 911345. There are four independent molecules in the unit cell with highly disordered CHO groups.

*Crystal data for **29***

(Obtained from toluene): $C_{20}H_{22}N_2O_2$, M = 257.33, space group $P2_1/n$ (monoclinic), a = 10.1751(6), b = 19.9254(11), c = 15.8690(9) Å, β = 95.633 (1)°, V = 3201.8(3) Å^3, Z = 8, D_c = 1.338 g cm^{-3}, μ(Mo-K_α) = 0.087 mm^{-1}, 120 K, 36 695 reflections collected, 9241 unique (R_{int} = 0.0522), 4348 reflections with $I > 2\sigma(I)$, 433 parameters, R_1 = 0.0508, wR_2 (all data) = 0.0760. CCDC reference number 911346. There are two independent molecules in the unit cell.

*Crystal data for **36***

(Obtained from acetone): $C_{26}H_{14}N_4O_4$, M = 446.41, space group $P2_1/n$ (monoclinic), a = 16.778(3), b = 7.692(2), c = 17.044(3) Å, β = 111.96(3)°, V = 2040.0(7) Å^3, Z = 4, D_c = 1.453 g cm^{-3}, μ(Mo-K_α) = 0.101 mm^{-1}, 293 K, 4028 reflections collected, 3059 unique (R_{int} = 0.0522), 2128 reflections with $I > 2\sigma(I)$, 364 parameters, R_1 = 0.0367, wR_2 (all data) = 0.0938. CCDC reference number 911348.

RESULTS AND DISCUSSION

Solution measurements

We have first studied sterically unhindered *p*-nitroanilines represented by structures **6–9** including *N*-anion **10**, which, similar to other *N*-anions described in this work, were generated in solution with the help of KOH/DMSO system (Table 1). As seen, the selected criteria ($^3J_{2,3}$ constants and λ_{max} of long-wave absorption bands) are indeed in line with the expected electron-donating trend of the amino groups:

$$NHAc < NH_2 < NHMe < NMe_2 < NMe^-$$

This sequence is in accord with their Hammett constants, σ_p,[19] as well as with other experimental and theoretical parameters.[8,35]

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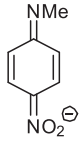
At the same time, no strict correlation is observed between the $^3J_{2,3}$ constants and the $\delta_{H\text{-}3}$ and $\delta_{H\text{-}2}$ chemical shifts as well as with the difference between them ($\Delta\delta$ values). Nevertheless, a general tendency of decreasing $\delta_{H\text{-}3}$ and $\delta_{H\text{-}2}$ values and increasing the $\Delta\delta$ parameter is present as the electron donor ability of amino group grows.[8] A position of the NMe^- group in the aforementioned raw as the strongest electron donor is confirmed by the corresponding $^3J_{2,3}$ constant (~10 Hz), which leaves no doubt of a significant contribution of quinoid structure **10a** into the resonance hybrid.



10a

On going from *p*-nitroanilines **3** to simple naphthalene derivatives **4**, along with more extended π-conjugated system, two kinds of repulsive *peri*-interactions appears: between the amino groups and between the nitro group and the H-5 hydrogen. Hence, the trend found in the benzene series is not expected to repeat here in detail.

Table 2 indicates that there is no dependence of $\delta_{H\text{-}3}$ ($\delta_{H\text{-}2}$) or $\Delta\delta$ values on the extent of through-conjugation in molecules **4**. However, irrespectively of the substituents in the naphthalene core, a correlation exists when $^3J_{2,3}$ and λ_{max} descriptors are considered. The picryl group, taken as the extended variant of a nitro function, turned out to be the worst acceptor from the naphthalene α position (cf. **11** and **14**). This is clearly due to the acoplanarity of the trinitrophenyl substituent and the naphthalene moiety (see the next section) so that virtually only the inductive component of the electron-withdrawing effect of this group persists. Meanwhile, the coplanarity of functional groups alone is not enough, as the record-holders in Table 2 are compounds **14** and **15** with bulky dialkylamino groups but not the expected dihydroperimidine **13**.

On the whole, the following quite good relationships are found between the $^3J_{2,3}$ and λ_{max} values (Tables 1 and 2; *n*, number of points, R^2, square correlation coefficient):

$$(4\text{–nitroanilines}) \quad {}^3J_{2,3} = 136.56\lambda_{max} - 880.54, n = 5, \quad R^2 = 0.9485 \qquad (1)$$

$$(1,8\text{–diamino–4–}R\text{–naphthalenes}) \; {}^3J_{2,3} = 142.01\lambda_{max} - 826.01, \; n = 5, R^2 = 0.9925 \qquad (2)$$

Comparative studies of dinitronaphthalene and dinitroperimidine derivatives **16–27** seemed especially interesting along with *peri*-dialdehydes **28**, **29** having less sterically demanded[18] CHO groups. All these molecules (Table 3) reveal no signs of desymmetrization in solution, showing a set of two doublets in the aromatic region of their ^{1}H NMR spectra as in the case of *p*-nitroanilines. *A priori* this could not be expected for perimidine **16** and mono-*N*-deprotonated diamine **21** (anion **25**). Obviously, in these molecules, fast intermolecular (for **16**) and intramolecular (for **25**) prototropism lead to the signal averaging in the spectra. The $[NHN]^-$ hydrogen bond in **25** appears at δ_H 9.6 ppm compared with δ_H 7.6 ppm from the two NH protons in **21**. Other proton NMR parameters of monoanion **25** are merely intermediate between those of diamine **21** and dianion **27**.

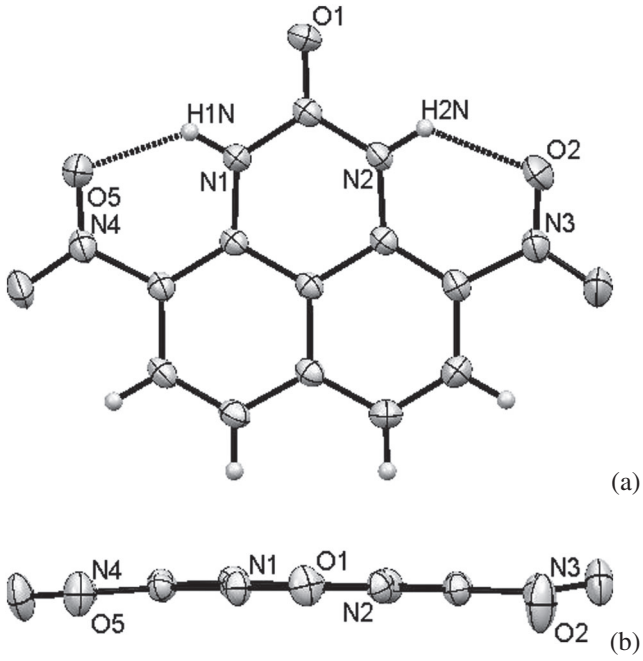


Figure 3. (a) Single-crystal X-ray structure of cyclic urea **17-*ortho*** (30% probability level, intramolecular H-bonds are shown). (b) View along the naphthalene central bond showing almost complete flatness of the molecule

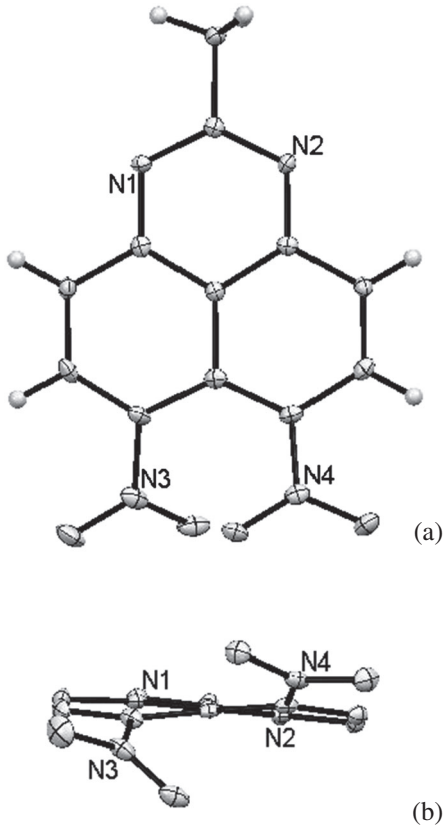


Figure 4. (a) Single-crystal X-ray structure of dinitro substituted perimidine *N*-anion **22** (30% probability level, cationic part and water molecules are not shown). (b) View along the naphthalene central bond with the nitro groups directed to the viewer

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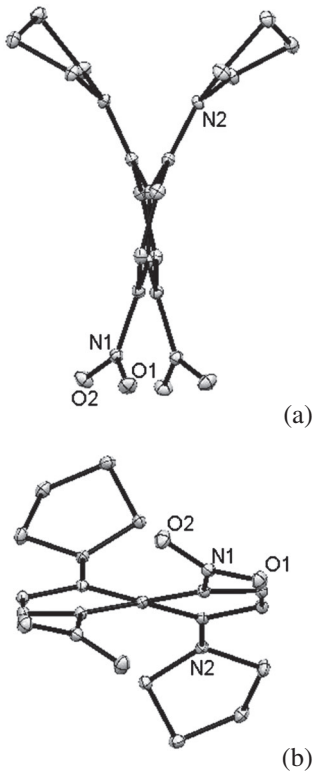
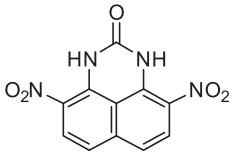
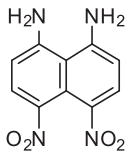


Figure 5. Single-crystal X-ray structure of dinitronaphthalene **24** (30% probability level, hydrogen atoms are omitted for clarity). (a) Side view and (b) view along the naphthalene central bond showing severe twisting of the aromatic moiety

Positions of other NH fragments to mention are δ_H(NH): 12.6 (**16**), 11.6 (**17**), and 11.0 ppm (**17-*ortho***). Isomers **17** and **17-*ortho*** were obtained by us on dinitration of 1*H*-perimidine-2-one, an easily available naphthalene-fused urea. Although less soluble isomer **17** prevailed, it was not easy to distinguish between them because of close physical appearance and ^{1}H NMR patterns. We, therefore, subjected **17-*ortho*** to X-ray diffraction analysis, which confirmed the arrangement of functional groups and revealed strong intramolecular H-bonding (see the next section).

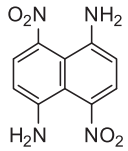


17-*ortho*

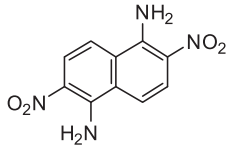


30

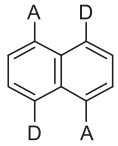
Unfortunately, we were unable to prepare for this work 1,8-diamino-4,5-dinitronaphthalene (**30**), the still unknown parent system of type **2**. Treatment of perimidine-2-one **17** with the excess of KOH in DMSO under short reflux (~190 °C) or at ambient temperature for 45 days gave nothing but dianion **26**, which is stable under these conditions (this approach, however, quite easily transforms **18** into **21**). No hydrolysis was observed on dissolution of **17** in conc. H_2SO_4 (24 h at 22 °C). Therefore, the simplest structure in our hands was dinitrodiamine **21**, which we managed to convert into **19**, **20**, **25**, and **27**.



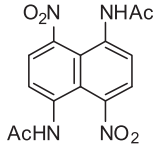
31



32



33



34

Interestingly, *anti*-analog of **30**, compound **31** was claimed to possess very high $^3J_{2,3}$ value (10 Hz),[36] but its structure was lately disproved as being in fact the 2,6-dinitro isomer **32**.[26] In addition, the D-π-A molecules of type **33** are much worse platforms for effective π-conjugation. For example, dinitrodiamide **34** forms almost colorless crystals from DMF and has $^3J_{2,3} = 9$ Hz[36] (we measured 8.1 Hz).[26]

We have selected the $^3J_{2,3}$ NMR parameter as the main

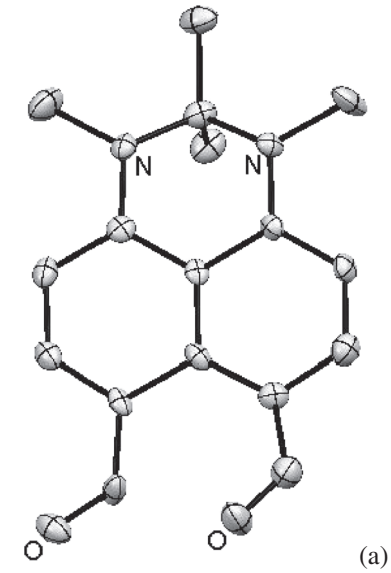


Figure 6. (a) Single-crystal X-ray structure of dialdehyde **28** (30% probability level, hydrogen atoms are omitted for clarity). (b) View approximately along the naphthalene central bond with the CHO groups directed to the viewer

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frame of reference to arrange the nitro and formyl derivatives in accordance with the degree of conjugation (Table 3) and at the same time have excluded compounds **16**, **17**, **22**, and **26** from consideration. The problem is that the NMR concentrations are generally by 10^2–10^3 times higher than those usually employed for UV–Vis measurements. As a result, for rather strong NH-acids **16** and **17** (they are soluble in aqueous Na_2CO_3), a partial ionization in DMSO is possible causing discrepancies in the UV–Vis trend observed for the neutral compounds. Already ionized species such as **22** and **26** also fall out of the correlation demonstrating anomalous bathochromic shift of the long-wave absorption bands if compared with the compounds close in $^3J_{2,3}$ constants. This can be assigned to some extra delocalization of the negative charge via the internitrogen bridge (the μ-C-2 atom). With these exceptions, the following correlation was found for the rest of dinitronaphthalenes:

$$(1,8\text{–diamino–}4,5\text{–dinitronaphthalenes}) \qquad (3)$$
$$^3J_{2,3} = 235.78\lambda_{max} - 1695.7, n = 8, R^2 = 0.9656$$

As seen, the correlation is quite good, and the worse points are those corresponding to anions **25** and **27**.

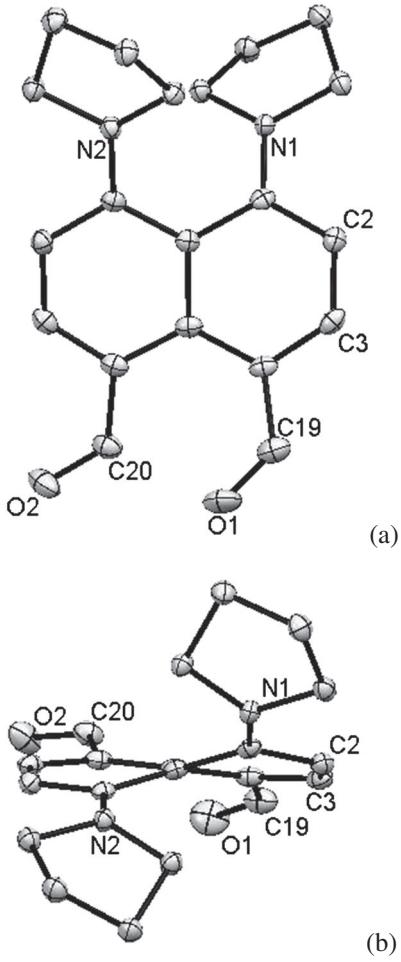
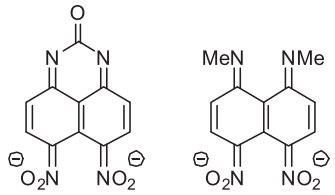


Figure 7. (a) Single-crystal X-ray structure of dialdehyde **29** (30% probability level, hydrogen atoms are omitted for clarity). (b) View along the naphthalene central bond showing twisting of the molecule

Tables 2 and 3 clearly demonstrate that, if the diamino parts of the push–pull molecules are similar, the π-acceptor ability of the two *peri*-NO_2 groups in **2** is almost the same as that of one α-NO_2 group in **4** with slight predominance of the latter (compare pairs **12**/**18**, **13**/**19**, **14**/**23**, and **15**/**24**). Hence, as representatives of the R_2N-π-NO_2 systems, motifs **2** and **4** are close in function and, in the terms of UV–Vis absorption, both surpass their benzene counterparts **3** because of the intrinsically longer conjugation chains. As to the $^3J_{2,3}$ criterion, despite of the notable contribution of resonance forms **26a** and **27a**, the bond order redistribution in **2** and **4** is not as effective as in **3** (see the next section).



26a **27a**

As it was already mentioned, neutral perimidines **16–20**, unless they are converted into anionic species **22** and **26**, are generally less effective for through-conjugation than *peri*-diamines **21**, **23**, and **24**. This conclusion is spread on dialdehydes **28** and **29** (Table 3). On the whole, the best donors from *peri*-positions are pyrrolidin-1-yl and methylamido groups.

Structural considerations

One of the obvious consequences of intramolecular charge transfer in the D-π-A push–pull molecules is the bond length redistribution on going from the non-through-conjugated (aromatic) to the fully conjugated (quinoid) structure. This transition requires both the donor and acceptor groups to be coplanar with the arylidene π-bridge.[8,37,38] Whereas this requirement is nicely fulfilled for simple 4-nitroanilines (structural data relevant for the illustration of the key bonds length alternation and acoplanarity, in particular φ values, are available for **7–9**, see

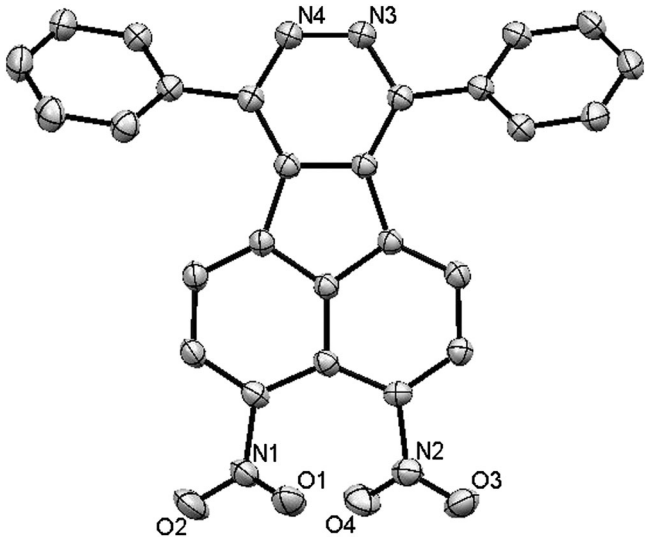


Figure 8. Single-crystal X-ray structure of pyridazine **36** (30% probability level, hydrogen atoms are omitted for clarity)

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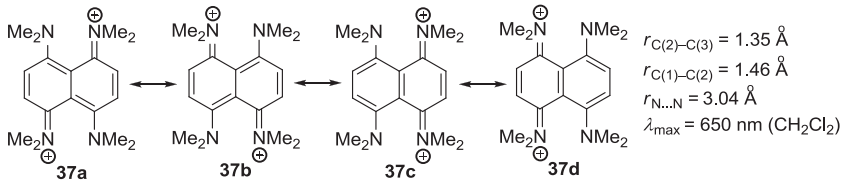
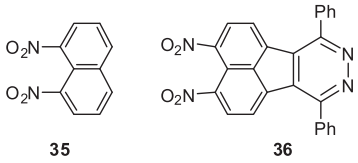


Scheme 2. Bond alternation and some properties of dication **37**

Table 4 for details), hindered nitroaromatics[39] display notable twisting of the nitro groups (picryl group in the case of **11**) and even aromatic moieties (Figs. 1–8). Thus, for parent 1,8-dinitronaphthalene **35** and its more complex derivative **36** (in the latter, the nitro groups are by 5% more distant, Table 4), the torsion angles φ are 43° and 39°, respectively (compare with $\varphi = 36°$ for dinitroperimidine **16**, Fig. 2).



It should be emphasized further that φ values in naphthalene derivatives may come to the level of benzenes **3** (that is close to coplanarity) in two distinct cases: (i) intramolecular hydrogen bonding (as in the case of flat H-bonded molecule **17-*ortho***, Fig. 5) and (2) strong through-conjugation (as in the case of pyrrolidino derivative **15**, Fig. 3), which is accompanied by notable distortion of the aromatic π-system expressed by ∠ABCD and $r_{N(1)...N(1)}$ (compare data for **14** and **15**, Table 4). Obviously, this molecular distortion is energetically favorable because of decreasing intramolecular Coulombic repulsion and steric strain.

Transition from **2** to **2a** also requires a contraction of the C(β)–C(β′) aromatic bond in the naphthalene fragment [uniformly marked here as C(2)–C(3)], which should be in close relation with the $^3J_{2,3}$ values determined for the same bond. This is however only roughly true because of the different media (crystal field and solution) and the different atoms used to extract the $r_{C(2)–C(3)}$ and $^3J_{2,3}$ parameters (carbon and hydrogen atoms, respectively). Anyhow, a general trend for the shrinkage of this bond up to 1.37 Å in benzene **3** and naphthalene **4** push–pull molecules carrying the most electron-donating amino groups (NHMe, NMe_2, and pyrrolidino) is easily seen (Table 4). Thus, all the C(2)–C(3) bonds are notably shorter than those in the nonconjugated *peri*-dinitronaphthalenes **35** and **36** or in compounds with the nitro groups placed in other positions (**11**, **17-*ortho***). However, the $r_{C(2)–C(3)}$ values in **14**, **15**, and **22** (1.37 Å) followed by **23** and **24** (1.38 Å) are still rather far from the purely quinoid bonds in naphthalene-1,4,5,8-tetrone ($r_{C(2)–C(3)} = 1.32$ Å)[40] but quite close to that in dication **37**, a product of two-electron oxidation of 1,4,5,8-tetrakis(dimethylamino)naphthalene (Scheme 2).[41]

In line with the shortening of the C(2)–C(3) bonds are the lengths of the N(1)–C(1) bonds, also reflecting the resonance interaction of the amino nitrogens with the aromatic rings (Table 4). Again, in the solid, *N*,*N*′-bridged compounds, even in the anionic form, possess longer $r_{N(1)–C(1)}$ distances than the *N*,*N*-dialkylated (compare **16** and **22** with **23** and **24**, see also dialdehydes **28** and **29**). The $r_{N(1)–C(1)}$ values become minimal (~1.35 Å) for compounds with the pyrrolidino groups (**15**, **24**, and **29**). Moreover, di(pyrrolidino)naphthalene **24** demonstrates record twisting of the naphthalene core (27°, Fig. 7), the highest value registered so far for 1,4,5,8-tetrasubstituted naphthalenes.[18,42] At the same time, there is no doubt that the internal twisting of molecules **15**, **24**, and **29** (a conjugation-induced chirality) is preserved in solution, because the CH_2 fragments in their room temperature ^{1}H NMR spectra are displayed as six to eight multiplets (four multiplets for compound **15**, see the Experimental part). Hence, we may conclude that the pyrrolidin-1-yl groups, even being placed in sterically hindered positions, are potent electron-donating substituents if compared with the NMe_2 functions.[43]

Finally, the resonance π-interaction between the electron donor and acceptor groups in the solid decreases on going from **4** to **2**, yet all structures demonstrate a strong bond alternation within the naphthalene skeleton.

CONCLUSIONS

In summary, using simple and adequate criteria, we have quantitatively compared the through-conjugation in 4-nitroanilines and 1,8-diamino-4-nitronaphthalenes with that of 12 1,8-diamino-4,5-dinitronaphthalenes, the widest set of sterically hindered A_2,D_2-naphthalenes published to date. The selected descriptors ($^3J_{2,3}$ constants and λ_{max} of long-wave absorption bands) reach their maximum in case of pyrrolidin-1-yl derivatives and methylamido anions, that is, for compounds possessing the highest degree of π-conjugation. The data received (both in solution and in the solid state), apart from the estimation of *peri*-interaction phenomena for the nitro and amino groups, may be of help to foresee further steps enhancing the donor–acceptor interaction in D-π-A arenes along with the possible limits in structure variations of organic compounds.

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