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Synthesis and Spectral Properties of Autocomplexes of the Nitroquinoline Series

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Abstract—A number of new NH-bridged nitroquinoline derivatives with intramolecular charge transfer (autocomplexes) were synthesized starting from 8-chloro-5,7-dinitroquinoline and aromatic N,O-heterocyclic amines characterized by different donor powers and substitution patterns. The charge transfer in their molecules may occur via both direct polar conjugation through the bond sequence including the bridging nitrogen atom and through space between spatially close molecular fragments (contact charge transfer).

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Organic compounds with intramolecular charge transfer (so-called autocomplexes), whose molecules contain simultaneously electron-donor and electron-acceptor fragments separated by a bridging moiety (spacer), are the most appropriate and reliable model systems for studying various intramolecular interactions [1]. Autocomplexes possess interesting electrophysical and optical properties [2, 3] which underlie their wide application in practice, specifically as materials for nonlinear optical devices, organic semiconductors, and photosensitizers.

While performing systematic studies on the synthesis of a large series of autocomplexes with a one-membered NH bridge and donor–acceptor interactions therein [4–13], we found that charge transfer in these compounds can occur via both direct polar conjugation along the bond sequence including the bridging nitrogen atom and through-space donor-acceptor interaction between molecular fragments (contact charge transfer). The relations holding in the charge transfer were established by analysis of the spectral data which were interpreted in terms of an empirical method [14]; this method allowed us to determine the number and origin of absorption bands in the electronic spectra of polysubstituted donor–acceptor benzene analogs without invoking quantum-chemical calculations.

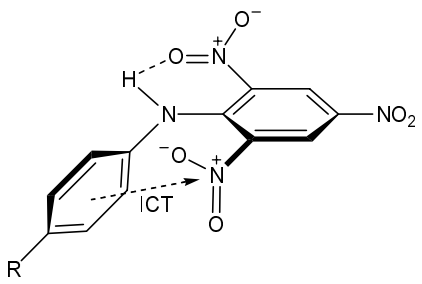


Fig. 1. Intramolecular charge transfer through space (contact charge transfer) between spatially close molecular fragments in autocomplexes of the trinitrobenzene series.

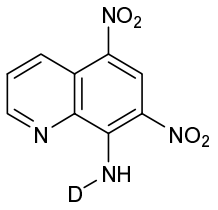
For example, charge transfer in autocomplexes of the 1,3,5-trinitrobenzene series having donor fragments of different natures and powers [4–9] occurs in two ways: (1) along the conjugation chain from the donor fragment to the *para*-nitro group ($CT_{NH}^{p\text{-}NO_2}$ or *para* transition) and (2) from the donor fragment to the planar *ortho*-nitro group which is linked to the bridging NH group through intramolecular hydrogen bond ($CT_{NH}^{o\text{-}NO_2}$ or *ortho* transition). According to the X-ray diffraction data [6, 7], the second *o*-NO_2 group is forced out from the plane of the acceptor trinitrophenyl ring, and it appears spatially close to the donor fragment, though their planes are not parallel; as a result, the molecule adopts a conformation in which that nitro group hangs over the donor ring. Such conformation is favorable for interaction between the above fragments and intramolecular charge transfer (ICT) through space (contact charge transfer, Fig. 1). In fact, the electronic absorption spectra of these complexes contain three bands corresponding to $CT_{NH}^{p\text{-}NO_2}$, $CT_{NH}^{o\text{-}NO_2}$, and CCT. On the other hand, the presence of two *ortho*-nitro groups in the acceptor fragment could

[†] Deceased.

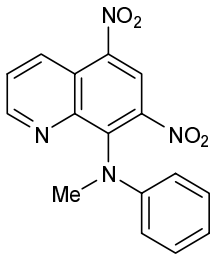
give rise to the second *ortho* transition through the conjugation chain including the *o*-NO_2 group which is already involved in CCT. However, we detected no additional *ortho*-transition band in the electronic spectra of 1,3,5-trinitrobenzene complexes, despite variation of donor fragments over a wide range of donor power. The question arises as to whether the second *ortho* transition is possible in principle or its intensity is so weak that it is obscured by other transitions.

While developing studies in this line, we focused on the synthesis and spectral properties of analogous dinitroquinoline derivatives which possess only one *ortho*-nitro group and the same set of donor components as that examined previously.

Compounds **I**–**XX** were synthesized by heating equimolar amounts of 8-chloro-5,7-dinitroquinoline and the corresponding amine in appropriate solvent (acetone, chloroform, or alcohol) under reflux. Initial 8-chloro-5,7-dinitroquinoline was prepared from 5,7-dinitroquinolin-8-ol, and the latter was obtained by nitration of quinolin-8-ol according to the procedures described in [15–17]. Except for compound **II**, no other dinitroquinoline derivatives were reported previously; moreover, amine **II** was not studied as autocomplex but as ligand for the synthesis of metal chelates [16].



I–XIX



XX

I, D = 4-$NO_2C_6H_4$; **II**, D = Ph; **III**, D = 4-IC_6H_4; **IV**, D = 4-MeC_6H_4; **V**, D = 4-PhC_6H_4; **VI**, D = 3,4-$Me_2C_6H_3$; **VII**, D = 1-naphthyl; **VIII**, D = 4-$MeOC_6H_4$; **IX**, D = 2-naphthyl; **X**, D = dibenzo[*b*,*d*]furan-2-yl; **XI**, D = 9*H*-fluoren-2-yl; **XII**, D = *N*-methylcarbazol-3-yl; **XIII**, D = 2-anthryl; **XIV**, D = 5-methoxyquinolin-8-yl; **XV**, D = 4-$PhNHC_6H_4$; **XVI**, D = 4-$Me_2NC_6H_4$; **XVII**, D = 4-Ph_2N-C_6H_4; **XVIII**, D = 2-cyclopropylphenyl; **XIX**, D = 4-phenylquinolin-8-yl.

The structure of compounds **I**–**XX** was confirmed by the analytical and spectral data (Tables 1, 2). The IR spectra of **I**–**XX** in KBr contained absorption bands belonging to antisymmetric and symmetric stretching vibrations of the NO_2 groups linked to the aromatic ring (1570–1530 and 1340–1290 cm^{-1}, respectively), bands due to vibrations of C–H bonds in the quinoline fragment (3100–2900 cm^{-1}), and N–H stretching vibration band located in the region 3280–3110 cm^{-1}, depending on the donor power of the D fragment. The ^1H NMR spectra of the products were consistent with the assumed structures; the NH signal appeared at δ 9.5–10.3 ppm, each proton in the pyridine ring gave a doublet of doublets in the region δ 7.77–9.5 ppm, and the signal located at δ 9.11–9.25 ppm was assigned to the 6-H proton (in the position between the two nitro groups). All amines **I**–**XX** were isolated as crystalline substances whose color varied from light yellow to dark red (almost black), depending on the nature of the donor fragment.

The most useful information on intramolecular charge transfer and its nature can be obtained by spectral studies. The electronic absorption spectra of compounds **I**–**XX** were measured from solutions in chloroform with concentrations of 10^{-3} to 10^{-4} M. The absorption bands were assigned using an empirical method [14] which implies decomposition of a molecule into initial polar chromophoric fragments. Table 1 lists the positions of the experimental absorption maxima (λ_{max}, nm), molar absorption coefficients (ε, $l mol^{-1} cm^{-1}$) of the CT bands, their assignment according to [14], published [18, 19] ionization energies (E_I, eV) of model donor fragments, and ICT energies (E_{ICT}, eV) of autocomplexes **I**–**XX**, calculated by formula (1) [20].

$$E_{ICT} = h\nu_{ICT} = 1239.81/\lambda_{max}. \quad (1)$$

According to [14], the electronic spectra of **I**–**XX** should contain absorption bands corresponding to charge-transfer transitions (in the order of decreasing excitation energy) from the donor fragment NHD to the acceptor *p*-NO_2 group (*para*-band), from NHD to *o*-NO_2 (*ortho*-band), and from NHD to the *o*-NO_2 group forced out from the acceptor ring plane (CCT). All compounds **I**–**XX** display in the experimental electronic spectra (Table 1) a long-wave maximum at λ 420–490 nm; as might be expected, this maximum shifts to longer wavelengths as the donor power of the NHD fragment increases. However, in the spectra of autocomplexes **I**–**XI** having weak donor components the long-wave absorption bands are broadened (obviously, these bands have a complex origin) and are characterized by anomalously high intensities. Presumably, these bands are superpositions of several charge-transfer bands, including both *ortho*-transitions and CCT between spatially close *o*-NO_2 group and donor

Table 1. Electronic absorption spectra of autocomplexes **I**–**XX** in $CHCl_3$ ($c = 10^{-3}$–10^{-4} M), ionization energies (E_I, eV) of the donor fragments, and energies of intramolecular charge transfer (E_{ICT}, eV)

Compound no.	E_{ICT}, eV	E_I, eV	λ_{max}, nm (ε)			
			$CT^{p\text{-}NO_2}_{NHD}$	$CT^{o\text{-}NO_2}_{NHD}$	$CT^{o\text{-}NO_2}_{NHD}$ + ICT	ICT
I	2.96	9.85	294 (18150)		419 (21190)	
II	2.97	9.25	293 (10690)		417 (16100)	
III	2.98	8.78–9.75	291 (14220)		416 (20950)	
IV	2.96	8.82	290 (14390)		419 (19770)	
V	2.86	8.27	271 (33410)		433 (22430)	
VI	2.97	8.27	290 (11720)		418 (17930)	
VII	2.97	8.26	289 (22390)		417 (20650)	
VIII	2.94	8.22	287 (14120)		422 (19250)	
IX	2.92	8.14	289 (18420)		425 (19400)	
X	2.82	7.90	280 (28800)		440 (15750)	
XI	2.80	7.89	283 (17540)		443 (14230)	
XII	2.74	7.60	300 (25800)	334 (11360)		453 (15480)
XIII	2.69	7.40	290 (11500)	330 (8250)		461 (14730)
XIV	2.65	7.38	261 (48370)	395 (11720)		467 (10140)
XV	2.70	7.30	292 (32310)		460 (16640)	
XVI	2.55	7.14	330 (8150)	372 (7150)		486 (10740)
XVII	2.51	7.03	303 (35830)	392 (13300)		494 (14410)
XVIII			291 (11080)		417 (17480)	
XIX			300 (16980)	410 (19040)		452 (24700)
XX			300 (10300)	410 (4390)		490 (5720)

fragment. In the spectra of compounds **XII**–**XVII** with fairly strong donor substituents, both these transitions appear separately. Replacement of hydrogen in the NH bridging group by methyl radical (compound **XX**) considerably enhances the donor power of the phenylamino group, and the spectrum of **XX** contains clearly resolved *ortho*-band and that corresponding to CCT.

Difficulties in the interpretation of complex maxima covering several transitions may be overcome using the second derivative of the absorption spectra with respect to wavelength in a narrow spectral region [21]. The presence of two unresolved bands in an electronic spectrum follows from the appearance in the second derivative of two negative maxima or from asymmetry of positive satellites. We already used this procedure to interpret complex electronic spectra of autocomplexes of the 1,3,5-trinitrobenzene series [9]. As applied to compounds **I**–**XI**, the use of the second derivative technique allowed us in each case to isolate from one complex maximum two particular bands corresponding to charge transfer from the donor NHD fragment to the *o*-NO_2 group (*ortho*-band) and contact charge transfer. The results of band resolution are presented in Table 2.

In keeping with the definition of autocomplexes, their electronic absorption spectra should be characterized by a linear relation between the position of the long-wave maximum (i.e., the energy E_{ICT}) and model ionization potential of the corresponding donor fragment. In fact, such relation exists for the autocomplexes of the nitroquinoline series. However, the use of the spectral data for compounds **I**–**XI** (Table 2), which were obtained by resolution of the long-wave maximum according to the second derivative method, gives a poorer correlation ($r = 0.9012$) than that found for compounds **XII**–**XVII** which show a separate ICT band; the linear relation between E_{ICT} and E_I for compounds **XII**–**XVII** is characterized by a correlation coefficient r of 0.9788 (Fig. 2). The correlation equation (or the straight line shown in Fig. 2) may be used as calibration data for estimation of unknown ionization potentials of a number of donor fragments. In the

Table 2. Electronic absorption spectra of autocomplexes **I**–**XI**, **XV**, **XVIII**, and **XIX** in $CHCl_3$ ($c = 10^{-3}$–10^{-4} M), results of resolution of the long-wave absorption maximum by the second derivative method, ionization energies (E_I, eV) of the donor fragments, and intramolecular charge transfer energies (E_{ICT}, eV)

Compound no.	E_{ICT}, eV	E_I, eV	λ_{max}, nm (ε)		
			$CT_{NHD}^{p\text{-}NO_2}$	$CT_{NHD}^{o\text{-}NO_2}$	ICT
I	2.97	9.85	294 (18150)	372 (6700)	418 (16340)
II	2.90	9.25	293 (10690)	385 (7980)	427 (13590)
III	2.88	8.78–9.75	291 (14220)	384 (8990)	430 (16940)
IV	2.84	8.82	290 (14390)	392 (10990)	436 (16300)
V	2.83	8.27	271 (33410)	391 (7710)	439 (17120)
VI	2.82	8.27	290 (11720)	395 (8760)	440 (14450)
VII	2.84	8.26	289 (22390)	393 (7200)	437 (14990)
VIII	2.82	8.22	287 (14120)	398 (5760)	439 (14700)
IX	2.83	8.14	289 (18420)	391 (6810)	438 (16130)
X	2.76	7.90	280 (28800)	403 (3520)	450 (11840)
XI	2.73	7.89	283 (17540)	402 (4520)	454 (11180)
XV	2.42	7.30	292 (32310)	450 (9300)	512 (5500)
XVIII	2.86	8.72[a]	291 (11080)	392 (8180)	433 (14010)
XIX	2.74	7.36[a]	300 (16980)	410 (19040)	452 (24700)

[a] The ionization energy was determined by the calibration curve shown in Fig. 2.

present work we thus determined ionization potentials (Table 2) of the donor fragments in autocomplexes **XVIII** and **XIX**.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Thermo-Nikolet IR-200 Fourier-transform spectrometer (USA) at a resolution of 2 cm^{-1}; scan number 64. In some cases, internal reflection spectroscopy was used to avoid un-desirable absorption at about 3400 cm^{-1} (OH stretching vibrations) due to high hygroscopicity of KBr. The electronic absorption spectra were measured on a UNICAM Helios α spectrophotometer (Great Britain) from solutions in chloroform ($c = 10^{-3}$–10^{-4} M; resolution 2 nm, spectral range 200–800 nm, cell path length 0.1 cm); the spectra were obtained in a digital form and were processed using Origin program. The ^1H NMR spectra were recorded on a Varian VXR-400 instrument (400 MHz) using TMS as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using benzene, acetone, chloroform, and their mixtures as eluent.

p-Nitroaniline, aniline, *p*-iodoaniline, *p*-methylaniline, 3,4-dimethylaniline, naphthalen-1-amine, *p*-methoxyaniline, naphthalen-2-amine, dibenzo[*b*,*d*]-furan-2-amine, anthracene-2-amine, 5-methoxyquinolin-8-amine, 4-phenylquinolin-8-amine, *N*,*N*-dimethylbenzene-1,4-diamine, *N*-methylaniline, 2-cyclopropylaniline, and quinolin-8-ol were commercial products. Fluoren-2-amine was synthesized from *N*-(fluoren-2-

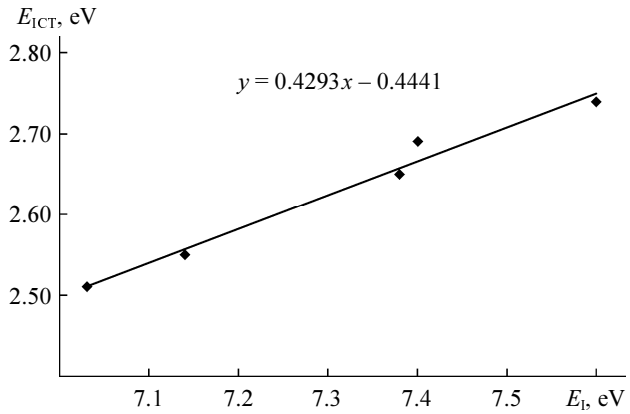


Fig. 2. Plot of the ionization energy of the donor fragment (E_I) versus intramolecular charge transfer energy (E_{ICT}) for autocomplexes **XII**–**XVII**.

yl)acetamide (preliminarily recrystallized from benzene) according to the procedure described in [22]. Yield 75%, light gray powder, mp 127–128°C; published data [22]: mp 129°C (from 50% alcohol). Biphenyl-4-amine, 9-methyl-9*H*-carbazol-3-amine, *N*,*N*-diphenylbenzene-1,4-diamine, and *N*-phenylbenzene-1,4-diamine were synthesized by reduction of the corresponding nitro compounds with hydrazine hydrate in the presence of Raney nickel [23] and were brought into reaction with 8-chloro-5,7-dinitroquinoline without isolation. Raney nickel was prepared as described in [24]. 5,7-Dinitroquinolin-8-ol was synthesized by a procedure reported in [15]. Yield 64%, light yellow–green powder, mp 276–277°C (decomp.); published data [16]: mp 276–279°C. 8-Chloro-5,7-dinitroquinoline was synthesized as described in [17]. Yield 87%, large transparent crystals, mp 157°C; published data: mp 158°C [16], 154°C [17]. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.27 d.d (1H, 2-H, $J_{2,3}$ = 4.0, $J_{2,4}$ = 1.5 Hz), 9.03 s (1H, 6-H), 8.93 d.d (1H, 4-H), 8.02 d.d (1H, 3-H, $J_{3,4}$ = 8.9 Hz) [17].

Synthesis of autocomplexes I–XX (*general procedure***).** A mixture of equimolar amounts of 8-chloro-5,7-dinitroquinoline and the corresponding amine in ethanol (or other organic solvent) was heated to the boiling point, cooled, and evaporated to 1/2 or 1/3 of the initial volume. The colored precipitate was filtered off and recrystallized from appropriate solvent. If the initial amine was taken as ammonium salt, it was preliminarily dissolved in 2–3 ml of water, 2 equiv of sodium carbonate and a required amount of solvent were added in succession, and the subsequent procedure was the same as above.

5,7-Dinitro-*N*-(4-nitrophenyl)quinolin-8-amine (I). Yield 40%, bright yellow needles, mp 240–242°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3233 (NH). Found, %: C 50.48; H 2.53. $C_{15}H_9N_5O_6$. Calculated, %: C 50.71; H 2.55.

5,7-Dinitro-*N*-phenylquinolin-8-amine (II) was synthesized by the procedure described in [16]. Yield 83%, large red–orange crystals, mp 196–198°C; published data [16]: mp 201°C.

***N*-(4-Iodophenyl)-5,7-dinitroquinolin-8-amine (III).** Yield 80.3%, fine light yellow needles, mp 220°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3178 (NH). Found, %: C 41.29; H 1.88; N 12.74. $C_{15}H_9IN_4O_4$. Calculated, %: C 41.31; H 2.08; N 12.85.

***N*-(4-Methylphenyl)-5,7-dinitroquinolin-8-amine (IV).** Yield 82.3%, bright orange needles, mp 201–202°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3227 (NH). Found, %: C 59.36; H 3.68; N 17.17. $C_{16}H_{12}N_4O_4$. Calculated, %: C 59.26; H 3.73; N 17.28.

***N*-(Biphenyl-4-yl)-5,7-dinitroquinolin-8-amine (V).** Yield 69%, fine brown needles, mp 222–224°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3243 (NH). Found, %: C 65.42; H 3.54; N 14.75. $C_{21}H_{14}N_4O_4$. Calculated, %: C 65.28; H 3.65; N 14.50.

***N*-(3,4-Dimethylphenyl)-5,7-dinitroquinolin-8-amine (VI).** Yield 60%, fine yellow–orange crystals, mp 202–204°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3230 (NH). Found, %: C 60.45; H 4.43. $C_{17}H_{14}N_4O_4$. Calculated, %: C 60.35; H 4.17.

***N*-(1-Naphthyl)-5,7-dinitroquinolin-8-amine (VII).** Yield 71%, large dark orange needles, mp 225–227°C (from acetone–alcohol, 1:1). IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3115 (NH). Found, %: C 63.57; H 3.50; N 15.41. $C_{19}H_{12}N_4O_4$. Calculated, %: C 63.33; H 3.36; N 15.55.

***N*-(4-Methoxyphenyl)-5,7-dinitroquinolin-8-amine (VIII).** Yield 88%, fine orange needles, mp 196–198°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3270 (NH). Found, %: C 56.50; N 3.36; N 16.55. $C_{16}H_{12}N_4O_5$. Calculated, %: C 56.47; H 3.55; N 16.46.

***N*-(2-Naphthyl)-5,7-dinitroquinolin-8-amine (IX).** Yield 80.5%, red–orange powder, mp 230–231°C (from EtOH). IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3240 (NH). Found, %: C 62.97; H 3.25; N 15.52. $C_{19}H_{12}N_4O_4$. Calculated, %: C 63.33; H 3.36; N 15.55.

***N*-(Dibenzo[*b*,*d*]furan-3-yl)-5,7-dinitroquinolin-8-amine (X).** Yield 82.3%, dark brown powder. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3254 (NH).

***N*-(9*H*-Fluoren-2-yl)-5,7-dinitroquinolin-8-amine (XI).** Yield 50.3%, red–brown powder, mp 252°C (decomp.). IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3252 (NH). Found, %: C 66.43; H 3.75; N 14.07. $C_{22}H_{14}N_4O_4$. Calculated %: C 66.33; H 3.54; N 14.06.

***N*-(5,7-Dinitroquinolin-8-yl)-9-methyl-9*H*-carbazol-3-amine (XII).** Yield 63%, orange powder,

mp 233–235°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3269 (NH). Found, %: C 63.91; H 3.43; N 17.24. $C_{22}H_{15}N_5O_4$. Calculated, %: C 63.92; H 3.66; N 16.94.

***N*-(2-Anthryl)-5,7-dinitroquinolin-8-amine (XIII).** Yield 72.5%, light orange powder, mp 260°C (decomp.). IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3205 (NH). Found, %: C 67.30; H 3.45; N 13.45. $C_{23}H_{14}N_4O_4$. Calculated, %: C 67.31; H 3.44; N 13.65.

***N*-(4-Methoxyquinolin-8-yl)-5,7-dinitroquinolin-8-amine (XIV).** Yield 67%, dark red powder, mp 265°C (sublimes). IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3222 (NH). Found, %: C 58.04; H 3.62. $C_{19}H_{13}N_5O_5$. Calculated, %: C 58.31; H 3.35.

***N*-(5,7-Dinitroquinolin-8-yl)-*N′*-phenylbenzene-1,4-diamine (XV).** Yield 74%, black–brown crystals, mp 148–150°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3182 (NH). Found, %: C 62.58; H 3.90; N 17.26. $C_{21}H_{15}N_5O_4$. Calculated, %: C 62.84; H 3.77; N 17.45.

***N′*-(5,7-Dinitroquinolin-8-yl)-*N*,*N*-dimethylbenzene-1,4-diamine (XVI).** Yield 96.5%, large dark red needles with metallic luster, mp 228–230°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3271 (NH). Found, %: C 57.54; H 4.41; N 19.87. $C_{17}H_{15}N_5O_4$. Calculated, %: C 57.79; H 4.28; N 19.81.

***N′*-(5,7-Dinitroquinolin-8-yl)-*N*,*N*-diphenylbenzene-1,4-diamine (XVII).** Yield 73.3%, black crystals, mp 185–187°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3235 (NH). Found, %: C 67.93; H 3.97; N 14.35. $C_{27}H_{19}N_5O_4$. Calculated, %: C 67.92; H 4.01; N 14.67.

***N*-(2-Cyclopropylphenyl)-5,7-dinitroquinolin-8-amine (XVIII).** Yield 73%, bright orange needles, mp 170–172°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3222 (NH). Found, %: C 61.81; H 4.03. $C_{18}H_{14}N_4O_4$. Calculated, %: C 61.71; H 4.03.

5,7-Dinitro-*N*-(5-phenylquinolin-8-yl)quinolin-8-amine (XIX). Yield 69%, red powder, mp 224–225°C. IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH), 3228 (NH). Found, %: C 66.68; H 3.32. $C_{24}H_{15}N_5O_4$. Calculated, %: C 65.90; H 3.46.

***N*-Methyl-5,7-dinitro-*N*-phenylquinolin-8-amine (XX).** Yield 83.3%, large dark red needles with metallic luster, mp 129–132°C (from ethanol). IR spectrum, ν, cm^{-1}: 1340–1290 (NO_2, sym.), 1570–1530 (NO_2, asym.), 3110–3040 (CH). Found, %: C 59.87; H 3.45; N 17.63. $C_{16}H_{12}N_4O_4$. Calculated, %: C 59.26; H 3.73; N 17.28.

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