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Polarity, Polarizability and Molecular Structure of Autocomplexes on the Basis of 1,4-Naphthoquinone

by V.V. Prezhdo[1], E.V. Ovsyankina[2] and O.V. Prezhdo[3]

[1]*Institute of Chemistry, Jan Kochanowski University, 25-020, Kielce, Poland*
[2]*Department of Organic Chemistry, Polytechnic Institute, Kharkov, Ukraine*
[3]*Department of Chemistry, University of Washington, Seattle WA 98195 , USA*

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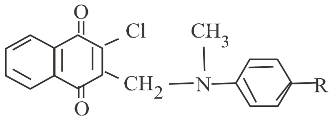
Experimental and theoretical investigation of molecular dipole moments and molar Kerr constants of 1,4-naphthoquinone based autocomplexes has been carried out. The results indicate the presence of intramolecular charge transfer of the n-π^* type. A correlation of the experimental values of molar Kerr constants with the σ^0-constants of substituents to the arylamine fragment of the autocomplexes has been established. Substituents to the electron donor fragment of the autocomplexes systematically affect the angle between the donor and acceptor fragments. *Ab initio* quantum-chemical calculations support the n-π^*-charge transfer structure and show notable changes in the charge on the nitrogen atom of the donor fragment due to complex formation.

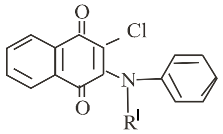
Key words: dipole moment, Kerr constant, autocomplexes, 1,4-naphthoquinone, intramolecular charge transfer, *ab initio* calculations

Intensive search for new chemical systems exhibiting donor-acceptor (DA) interactions has led to many important theoretical and practical conclusions [1,2]. Intramolecular DA complexes, or autocomplexes, where donor (D) and acceptor (A) fragments are connected through a molecular bridge bonds, constitute one of the main types of DA compounds. In autocomplexes the bridge is a structural part of the DA molecule. It severs the conjugation between D and A fragments and determines the spatial arrangement of the interacting D and A orbitals. Depending on the length of the molecular bridge in DA autocomplexes, DA interaction can be either intramolecular, directly through the bridge, or intermolecular, or both [3]. The intermolecular DA interaction can lead to formation of stable DA pairs. Considering the importance of intramolecular DA interactions in various chemical and biochemical processes as well as in design of substances with predetermined chemical, biological, or physical properties [3], the present work studies the relationship between intramolecular charge transfer (ICT) and molecular structure by electric properties of DA molecules.

DA complexes of the D-$(CH_2)_n$-A type with varying *n* are popular models in the studies of the role of the bridge size in DA interactions [6–9]. Several different mechanisms for the interaction between D and A species have been proposed for the first molecule in this series, D-CH_2-A. The ICT mechanism has been found most appropriate, and the D-CH_2-A molecule is usually treated as a DA autocomplex [3].



R = H (I), CH_3 (II), OCH_3 (III),
$N(CH_3)$ (IV), Br (V), $COOC_2H_5$ (VI)



R' = H (VII), CH_3 (VIII)

Autocomplexes I through VI together with the model compounds VII and VIII have been investigated previously with various physical-chemical techniques [3]. It has been shown that in condensed phases, depending on conditions, compounds I through VI can exhibit intermolecular charge transfer, for example in crystalline phase [10]. They can also exist in equilibrium between inter- and ICT structures, as is the case of concentrated solutions [11]. In moderately and strongly dilute solutions with concentrations 10^{-2}–10^{-3} mol/l and below, compounds I through VI exist as intramolecular autocomplexes. This conclusion is supported by the ICT spectral band in the region between 550 and 700 nm, and by the absence of the temperature dependence of molecular dipole moments between 25 and 65°C [6]. The oscillator strength $f_{D\to A}$ of the ICT transition band is used to quantify the extent of ICT [12]. In contrast to DA binary systems [13], in autocomplexes charge transfer (CT) does not proceed 100%. The ICT conformation, although the most stable, is only one of the possible conformations of an autocomplex. The energy of the ICT conformation grows with decreasing electron donor ability of the donor fragment of the autocomplex molecule, in particular, with increasing σ^0 constants of substituents R [12].

Now, CT properties of the ICT autocomplexes and the relationship between CT and molecular structure are investigated by the dipole moment and Kerr constant methods, which are often used for structural studies [14,15], as well as by quantum-chemical calculations.

EXPERIMENTAL

The autocomplexes are synthesized according to [3]. The dielectric measurements are carried out by the «Dipole» apparatus made by the Angarsk construction buerau, Russia. The «Dipole» apparatus is used to determine the dielectric permittivity (ε) and density (ρ) of dilute solutions (10^{-3} mol/l) of autocomplexes in benzene. Molar polarizabilities of the dissolved substances, extrapolated to infinite dilution $P_{2\infty}$, are calculated according to [16]. The obtained values of $\alpha_H = d\varepsilon/dN_2$, $\beta = d\rho/dN_2$, where N_2 is the molar fraction of the autocomplex, the molar polarization $P_{2\infty}$ of the dissolved substances extrapolated to infinite dilution and the deformation polarization P_D ($P_D = 1.1R_D$, where R_D is molar refraction coefficient), and the experimental molecular dipoles μ_{exp} are given in Table 1. The molecular dipoles calculated by the vector addition scheme, μ_{calc}, are based on the data of [17–20]. Kerr constants (B) of the autocomplex solutions are investigated using the apparatus and technique described in [21]. Refractive indices (n_D) are measured by refractometer IRF-23. Molar Kerr constants are calculated based on the experimental data according to [22]. The concentration dependencies of the measured parameters of the solutions are expressed in the form $\varepsilon = \varepsilon_1 (1 + \alpha_L\omega_2)$, $\rho = \rho_1 (1 + \beta_L \omega_2)$, $n = n_1(1 + \gamma\omega_2)$, $B = B_1(1 + \delta\omega_2)$, where ω_2 is mass fraction of the solute, and ε_1, ρ_1, n_1 and B_1 are the corresponding parameters of the solvent. Extrapolation to infinite dilution is carried out graphically. The values of $\alpha_L = d\varepsilon/d\omega_2$, $\beta_L = d\rho/d\omega_2$, $\delta = dB/d\omega_2$ and mK are given in Table 1. The index of refraction n remains essentially constant within the concentration range under investigation,. Therefore, it is assumed that $\gamma = 0$. Molar Kerr constants (mK_{calc}) are calculated by the tensor addition scheme, based on the data of [14,18–20]. *Ab initio* quantum chemical calculations are performed with the Gaussian 98 suite of programs, using the RHF method and a variety of basis sets [23]. The effect of the solvent is investigated by the SCI-PCM continuum solvent model [23].

Table 1. Experimental (benzene, 25°C) and calculated by vector and tensor addition schemes values of dipole moments (μ) and molar Kerr constants (mK) of the autocomplexes[a].

Compound	$\frac{\alpha_H}{\alpha_L}$	$\frac{\beta_H}{\beta_L}$	δ	$P_{2\infty}$, cm^3	P_D, cm^3	μ_{exp} D	mK_{exp} 10^{12}	φ^0	ψ^0	μ_{calc} D	mK_{calc} 10^{12}
I	$\frac{12.34}{1.59}$	$\frac{0.313}{0.170}$	38.6	258.2	92.65	2.84	152	40	70	3.0	157
II	$\frac{10.82}{1.34}$	$\frac{0.503}{0.112}$	25.2	235.6	97.77	2.59	103	50	70	2.7	98
III	$\frac{11.59}{1.40}$	$\frac{0.322}{0.094}$	12.8	255.6	99.55	2.76	54	60	50	2.9	50
IV	$\frac{11.50}{1.25}$	$\frac{0.295}{0.079}$	15.1	258.7	107.0	2.72	–71	70	60	2.8	–72
V	$\frac{24.30}{2.56}$	$\frac{0.429}{0.105}$	55.2	450.0	101.1	4.13	269	20	90	4.2	270
VI	$\frac{29.66}{3.22}$	$\frac{0.320}{0.070}$	27.5	527.7	106.3	4.54	124	40	80	4.4	129
VII	$\frac{17.33}{1.64}$	$\frac{0.389}{0.125}$	61.8	319.9	81.80	3.36	22.3	–	–	–	–
VIII	$\frac{11.07}{1.49}$	$\frac{0.777}{0.185}$	49.4	224.8	87.12	2.59	186	–	–	–	–

[a] α_L, α_H, β_H, β_L, δ, $P_{2\infty}$ and P_D are defined in the experimental part; φ^0 and ψ^0 are defined in the main text.

RESULTS AND DISCUSSION

Experimental molecular dipole moments and molar Kerr constants are given in Table 1. They are compared with the corresponding values calculated by the vector and tensor addition schemes for possible molecular isomers. Agreement between the experimental and calculated values for a given isomer indicates the most likely molecular structure [18].

Considering Brigleb-Stewart molecular models for the autocomplexes under study, it is feasible to assume two conformations with ICT. The first conformation is elongated with the possibility of CT from the lone electron pair of the nitrogen atom onto the acceptor fragment, *i.e.*, CT of the n–π* type. The second conformation is twisted with CT of the π–π* type. Several other conformations are also feasible, but are not likely to involve CT.

Molar Kerr constants and molecular dipole moments of each compound are expressed as functions of the rotation angle of the donor fragment φ around the C^2–N axis and of the rotation angle of the benzene ring ψ around the N-R axis, Fig. 1. The reference structure is defined by the conformer with the D and A fragments perpendicular to each other and oriented in the XOY and ZOY planes, respectively.

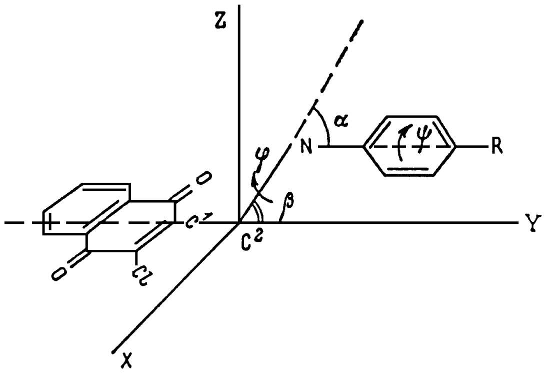


Figure 1. Molecular conformations of the autocomplex with diatomic (C_2 and N) bridge.

It has been shown [18,19] that direct polar conjugation significantly affects molecular polarizability ellipsoids in para-substituted aromatic compounds. In particular, electron donor substituents to the para position relative to the N,N-dimethylamino group increase pyramidality of the nitrogen atom and non-planarity of other molecular fragments [20]. The changes of the ellipsoid axes of molecular polarizability tensors take place in aromatic compounds of the *para*-N-C_6H_4–R type [18]. As the result, calculation of molar Kerr constants according to the tensor addition scheme based on bond polarizabilities fails to establish molecular structure. Instead, the tensor addition scheme is applied, based on polarizabilities of the whole molecular fragments. The polarizability ellipsoids of the D and A fragments of the autocomplexes are taken from [18,24]. Simultaneous comparison of molar Kerr constants and molecular dipole moments by the tensor and vector addition schemes relative to the experimental data produces the values given in Table 1. The changes in molecular polarizability ellipsoids in model compounds VII and VIII, due to direct conjugation between D and A fragments, hamper the utility of the tensor addition scheme, even that based on the fragment polarizabilities. The Kerr effect approach cannot be used for determination of the molecular structure of compounds VII and VIII.

Dreyding molecular models, constructed based on the derived values of the rotation angles φ and ψ, support the conclusion of the spectroscopic studies [11,25] that establish the n-π^* nature of CT from the amino-group donor to the naphthoquinone acceptor fragment of the autocomplexes. The nature of CT is further supported by the linear correlation between the experimental molar Kerr constants and substituent σ^0 constants [26]; these latter reflect the extent of transfer of polar effects through the CH_2 group that interrupts conjugation between the aromatic subsystems, Fig. 2. The only compound, that does not obey the σ^0-correlation, is compound VI. It contains the $COOC_2H_5$ group, whose interaction with the benzene ring is complex, and the calculated molar Kerr constants of compounds contained this group are inconsistent with the experimental ones [6]. Related to the correlation of Kerr constants with σ^0 constants is the correlation between σ^0 constants and the φ angle between the donor and acceptor species. The angle grows for stronger electron donor substituents, reflecting

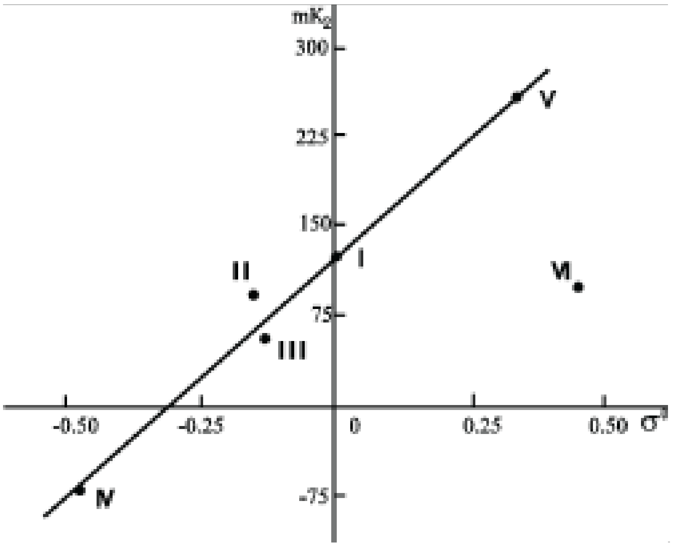


Figure 2. Correlation between molar Kerr constants (mK) of the autocomplexes and σ^0-constants of substituents (R). Autocomplex numbers correspond to Table 1.

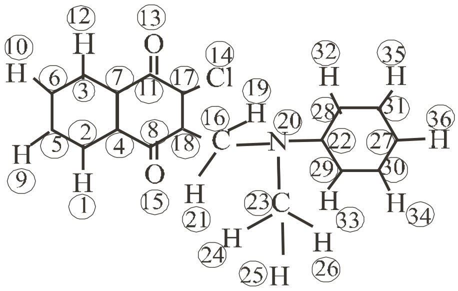
the increase of the interactions of the n-electrons of the nitrogen atom with the π-electrons of fragment A. As before, compound VI with R = $COOC_2H_5$ falls out of this correlation.

Ab initio quantum-chemical calculations support the existence of the n-π* CT structure. The calculations show that CT takes place both in the gas phase and in the solution, including benzene and aqueous solutions, Table 2. At the same time, the extent of CT varies in the presence of a solvent, and the charge distribution changes from gas phase to solution. In molecule I, Table 2, the nitrogen atom is least affected. Calculated by the continuum solvent model in an *ab initio* basis of moderate size, the Mulliken charge on the nitrogen atom is $q_N = -0.69565$ in the gas phase, –0.69560 in benzene and –0.69554 in water. Mulliken charges on other atoms of molecule I experience larger changes due to the solvents.

[9] shows by anode oxidation of 2-derivatives of 3-aryl-1,4-naphthoquinones that the CT structure is formed not only in the electron transfer case, but also during formation of cation-radicals. Electro-oxidation of autocomplexes of the type under study reveal electron acceptor behaviour of the arylamine fragment, that at the same time acts as electron donor inside the N,N-dimethylaniline fragment. The experimental results are supported by the quantum-chemical calculations presented here. Since the autocomplexes under study exhibit CT of the n-π*-type, the magnitude of the charge on the nitrogen atom (q_N) is indicative of the properties of the arylamine fragment. As evidenced by the data of Table 3 obtained with large *ab initio* basis sets, q_N in the N,N-dimethylaniline molecule becomes more positive when the molecule becomes the D fragment of the autocomplex. Moreover, even a single molecule of benzene solvent interacting with the autocomplex, Fig. 3, significantly enhances ICT. The q_N charge changes from 0.490 to 0.651 based on the RHF calculation in the

6-311++g** basis set. In contrast to the arylamine fragment, electro-reduction of the naphthoquinone fragment of the autocomplex is hampered [8] due to its π–acceptor role in the DA interaction.

Table 2. Atomic coordinates and Mulliken charges in autocomplex I calculated by RHF/6-31g*.



Atom	Coordinates			Mulliken Charge		
	X	Y	Z	Gas phase	In benzene	In water
H^1	–5.226819	0.540316	0.504872	0.259	0.266	0.267
C^2	–4.561399	–0.303185	0.357385	–0.183	–0.196	–0.197
C^3	–2.860452	–2.488989	–0.020308	–0.182	–0.195	–0.196
C^4	–3.207002	–0.096114	0.071724	–0.098	–0.095	–0.095
C^5	–5.063838	–1.604292	0.454280	–0.196	–0.209	–0.210
C^6	–4.213198	–2.696524	0.265586	–0.196	–0.208	–0.209
C^7	–2.357220	–1.187295	–0.117368	–0.100	–0.095	–0.095
C^8	–2.631839	1.296925	–0.039934	0.584	0.609	0.611
H^9	–6.114505	–1.765991	0.676638	0.226	0.252	0.254
H^{10}	–4.603079	–3.707333	0.340674	0.225	0.252	0.254
C^{11}	–0.898348	–0.931344	–0.424074	0.575	0.590	0.591
H^{12}	–2.207266	–3.342618	–0.165622	0.257	0.267	0.267
O^{13}	–3.347973	2.270552	0.125813	–0.528	–0.573	–0.576
Cl^{14}	–0.622028	3.143612	–0.454510	0.079	0.065	0.064
O^{15}	–0.143451	–1.878329	–0.575516	–0.547	–0.571	–0.573
C^{16}	1.095395	0.615721	–0.858710	–0.087	–0.097	–0.098
C^{17}	–1.202553	1.490298	–0.347480	–0.241	–0.238	–0.237
C^{18}	–0.376075	0.447995	–0.535649	–0.052	–0.038	–0.037
H^{19}	1.349082	–0.092599	–1.662618	0.211	0.220	0.221
N^{20}	1.929191	0.399008	0.324758	–0.696	–0.696	–0.696
H^{21}	1.341741	1.612771	–1.248200	0.205	0.211	0.212
C^{22}	3.176568	–0.115829	0.190986	0.294	0.293	0.293

Table 2 (continuation)

C^{23}	1.434285	0.765374	1.650905	–0.278	–0.287	–0.287
H^{24}	2.213630	0.687930	2.425175	0.190	0.197	0.197
H^{25}	0.609581	0.094768	1.934185	0.151	0.159	0.160
H^{26}	1.066364	1.802085	1.636312	0.170	0.173	0.173
C^{27}	5.763425	–1.155179	–0.092318	–0.214	–0.235	–0.236
C^{28}	3.365490	–1.403750	–0.322348	–0.237	–0.247	–0.247
C^{29}	4.287142	0.644880	0.571130	–0.226	–0.238	–0.239
C^{30}	5.577722	0.125655	0.435555	–0.198	–0.217	–0.218
C^{31}	4.656674	–1.918030	–0.473803	–0.200	–0.218	–0.219
H^{32}	2.512400	–2.013128	–0.599918	0.242	0.240	0.240
H^{33}	4.148845	1.645267	0.967492	0.200	0.217	0.218
H^{34}	6.436703	0.717264	0.738924	0.197	0.216	0.217
H^{35}	4.800006	–2.912473	–0.885439	0.199	0.216	0.217
H^{36}	6.766186	–1.556411	–0.204856	0.193	0.209	0.210

Table 3. Mulliken charges on the N atom (q_N) and molecular dipole moments (μ) of the individual molecules and autocomplex obtained by *ab initio* RHF calculations using several quantum-chemical basis sets.

Compound	Basis	q_N	μ_x, D	μ_y, D	μ_z, D	μ, D
N,N-dimethyl-aniline	STO-3g	–0.314	–0.6703	0.0149	–0.0186	0.6707
	6-31g*	–0.680	–0.8295	0.0242	–0.0363	0.8306
	6-311g	–0.826	–0.8798	0.0217	–0.0444	0.8812
	6-311+g*	0.565	–0.9191	0.0291	–0.0399	0.9204
	6-311++g**	0.273	–0.9499	0.0281	–0.0365	0.9510
Autocomplex I	STO-3g	–0.312	–1.5798	–2.4685	0.2695	2.9431
	6-31g*	–0.696	–2.0688	–2.3271	0.3681	3.1354
	6-311g	–0.834	–1.9840	–2.6720	0.4841	3.3631
	6-311+g*	0.771	–2.0482	–2.2195	0.3963	3.0460
	6-311++g**	0.490	–2.0450	–2.1983	0.3993	3.0289
Intermolecular complex between autocomplex I and benzene	STO-3g	–0.311	1.6234	–2.3319	–0.6460	2.9138
	6-31g*	–0.696	2.2879	–2.2718	–0.3767	3.2461
	6-311g	–0.696	2.2879	–2.2718	–0.3767	3.2461
	6-311+g*	0.994	2.2231	–2.1687	–0.4511	3.1383
	6-311++g**	0.651	2.2226	–2.1482	–0.4472	3.1232

Quantum-chemical results, including Mulliken charges and molecular dipole moments, are quite sensitive to the choice of the basis set, Table 3. Consider the N,N-dimethylaniline (DMA) part of autocomplex I. In isolated DMA the n-electrons of the nitrogen atom are conjugated only with the benzene ring . The charge q_N on the nitrogen atom changes as DMA becomes part of the complex. The predicted change $\Delta q_N = q_N(DMA) - q_N(I)$ grows significantly larger with increasing basis set, Fig. 4, curve I. The sensitivity of Δq_N to the basis set is even more pronounced in the complex of compound I with the benzene molecule, Fig. 4, curve II.

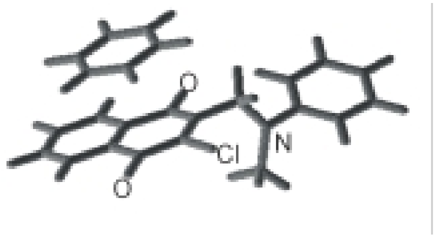


Figure 3. Minimum energy conformation of the intermolecular complex formed by the autocomplex and benzene molecule.

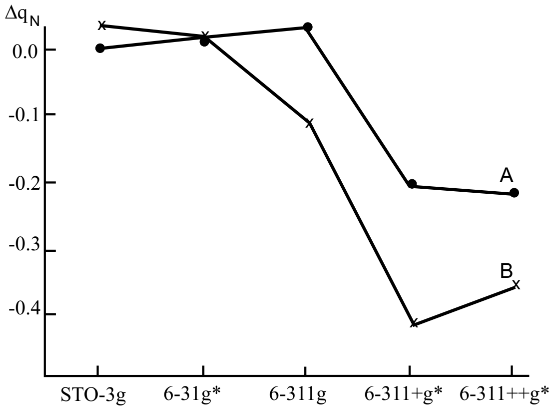


Figure 4. Change in the charge on the nitrogen atom (Δq_N) due to formation of autocomplex I (curve *A*) and to formation of intermolecular complex of compound I with benzene molecule (curve *B*) for different quantum-chemical *ab initio* basis sets.

The original application of quantum-chemical data to calculation of molar Kerr constants of simple molecules [27] is extended here to include autocomplexes. Table 4 presents molecular dipole moments and molar Kerr constants of the autocomplexes under study obtained by RHF in the 6-311++g** basis. The calculated dipole moments (Table 4) are in good agreement with the experimental data (Table 3) with three exceptions, compounds III, VI, and VIII. The agreement between the quantum-chemical and experimental molar Kerr constants is noticeably worse, apparently for two reasons. First, the experimental values of molar Kerr constants are very sensitive to solvent effects. As noted earlier, the autocomplex molecules strongly interact with molecules of the solvents, such as benzene, where solute-solvent intermolecular CT is observed. The molar Kerr constant sensitivity to solvent effects is evident from the experimental study of electronic absorption spectra [28]. Continuum solvent models, such as SCI-PCM, cannot be expected to reproduce solute-solvent CT. Only explicit molecular level consideration of the solvent can describe this effect. Second, ICT even in isolated molecules constitutes a challenge for the quantum-chemical methods at the mean-field level. Molecular dipole moments, that provide the basic criterion for CT and are least sensitive to the details of charge distribution, are predicted quite well. The higher order properties of the molecular charge distribution, that are responsible for the Kerr effect, require a more accurate treatment including electron

Table 4. Mulliken charges on the nitrogen atom (q_N), molecular dipole moments (μ), molecular polarizability tensors (b_{ij}), and molar Kerr constants (mK) of the autocomlpexes, calculated by the RHF quantum-chemical *ab initio* method in the 6-311++G**basis.

Compound	R	q_N	b_{xx}, Å^3	b_{yy}, Å^3	b_{zz}, Å^3	b_{xy}, Å^3	b_{xz}, Å^3	b_{yz}, Å^3	μ_x, D	μ_y, D	μ_z, D	μ, D	mK·10$^{12a)}$
I	H	0.490	43.044	36.299	20.235	–1.547	–1.911	1.575	–2.0450	–2.1983	0.3993	3.0289	160.4
II	CH_3	0.584	46.483	37.499	21.455	–1.692	–1.976	1.374	–1.4819	–2.4143	0.3822	2.8585	105.3
III	OCH_3	0.544	47.314	38.208	21.709	–2.057	–1.991	1.015	–1.9223	–2.7122	–0.0750	3.1811	55.0
IV	$N(CH_3)_2$	0.587	51.816	40.152	23.648	–1.776	–2.160	1.227	–0.1955	–2.8127	0.2281	2.8287	–75.2
V	Br	0.541	49.920	37.486	21.446	–1.809	–2.088	1.105	–3.9338	–1.9571	0.5803	4.4319	283.4
VI	$COOC_2H_5$	0.617	52.127	39.331	22.588	–1.774	–2.108	1.296	–3.7187	–0.5205	1.1842	4.0108	113.4
VII	–	0.755	40.834	34.381	20.883	–3.686	–1.302	–0.787	2.1674	–2.8973	0.7757	3.4005	27.3
VIII	–	0.842	44.952	35.075	25.285	–3.290	–1.294	–1.072	2.0863	–1.7115	0.7933	2.6841	198.2

[a] $mK = 3\pi N(\theta_1 + \theta_2)$, where θ_1 and θ_2 are anisotropic and dipole terms of molar Kerr constant, correspondingly, and N is Avogadro number.

$\theta_1 = (45\ kT)^{-1}\ (b_{xx} - b_{yy})^2 + (b_{yy} - b_{zz})^2 + (b_{zz} - b_{xx})^2 + (6b_{xy}^2 + b_{xz}^2 + b_{yz}^2)$;

$\theta_2 = (45\ k^2T^2)^{-1}\ [\mu_x^2(2b_{xx} - b_{yy} - b_{zz}) + \mu_y^2(2b_{yy} - b_{zz} - b_{xx}) + \mu_z^2(2b_{zz} - b_{xx} - b_{yy}) + 6(\mu_x\mu_y b_{xy} + \mu_x \mu_z b_{xz} + \mu_y\mu_z b_{yz})]$, where k is Boltzman constant, and T is T ^{0}K.

correlation. The autocomplexes investigated here exemplify the situation, where ICT only slightly changes molecular dipoles, but has a pronounced effect on the anisotropy of molecular polarizability [4].

CONCLUSIONS

CT of the n-π-type, that has been established earlier in 1,4-naphthoquinone based autocomplexes by spectroscopic techniques, is now confirmed by investigation of the electric properties. A linear correlation between the experimental molar Kerr constants of the autocomplexes with the σ^0-constants of the substituents R to the donor fragment of the molecules is observed. This correlation reflects the transfer of polar effects between the aromatic systems through the CH_2 bridge, that interrupts the π-conjugation. Stronger electron donor substituents gradually and justifiably increase the rotation angle φ of the donor fragment, due to the increasing coupling between the n-electrons of the nitrogen atom and the π-electrons of the acceptor fragment of the autocomplex molecules.

REFERENCES

1. Kampar V.E., *Usp. Khim.*, **51**, 185 (1982).
2. Neiland O.J., *Izv. AN Latv. SSR, ser. fiz i tekhn. nauk*, **6**, 63 (1981).
3. Freimanis J.F., Organic Compounds with Intermolecular Charge Transfer, Zinatne, Riga 1985 (in Rusian).
4. Prezhdo V.V. and Krainov I.P., Intermolecular Interactions and Electric Properties of Molecules, Osnova, Kharkov 1994 (in Rusian).
5. Fonseca T., Kim H.J. and Hynes J.T., *J. Mol. Liq.*, **60**, 161 (1994).
6. Prezhdo V.V., Khaschina M.V., Korobova M.V., Berestetskaya V.D., Freimanis J.F. and Dregeris J.J., *Zh. Obsch. Khim.*, **48**, 642 (1978).
7. Zalis S., Fiedler J., Pospisal I., Fanelli N. and Lanza C., *Microchem. J.,* **54**, 478 (1996).
8. Turovska B., Stradnis J., Strazdnis I., Logins J. and Dregeris J., *J. Electroanal. Chem.*, **394**, 229 (1995).
9. Turovska B., Stradnis J., Freimanis J., Strazdnis I., Logins J. and Dregeris J., *J. Electroanal. Chem.,* **414**, 221 (1996).
10. Schvets A.E., Bleidelis J.J. and Freimanis J.F., *Zh. Strukt. Khim.*, **1**, 415 (1975).
11. Freimanis J.F., *Izv. AN Latv. SSR, ser. fiz i tekhn. nauk*, **1**, 71 (1976).
12. Dregeris J.J., Malmanis A.J., Ignatovich L.G., Abolinsh J.J., Dumlis T.T., Lokmane E.J. and Freimanis J.F., *Zh. Obsch. Khim.*, **50**, 1148 (1980).
13. Vtyurina N.N. and Chmutova G.A., *Zh. Obsch. Khim.*, **48**, 2564 (1978).
14. Vereschagin A.N., Polarizability of Molecules, Nauka, Moscow 1980 (in Rusian).
15. Prezhdo O.V., Vaschenko E.V., Prezhdo V.V. and Puszko A., *J. Mol. Str.,* **471**, 1279 (1998).
16. Hedestrand G., *Z. Phys. Chem.*, **B2**, 428 (1929).
17. Minkin V.I., Osipov O.A. and Zhdanov Yu.A., Dipole Moments in Organic Chemistry, Khimia, Leningrad 1968 (in Rusian).
18. Vulfson S.G., Vereschagin A.N. and Arbuzov B.A., *DAN SSSR*, **209**, 885 (1973).
19. Vulfson S.G., Sorokina L.A., Kataeva L.M. and Vereschagin A.N., *DAN SSSR*, **216**, 837 (1974).
20. Kitaigorodskii A.I., Zorkii P.M. and Bel'skii V.K., Organic Compounds Structure. Data of X-ray Investigation, Nauka, Moscow 1980 (in Rusian).
21. Prezhdo V.V., Khaschina M.V. and Zamkov V.A, Electrooptic Investigations in Physic and Chemistry, Vyscha schkola, Kharkov 1982 (in Rusian).

22. Le Fevre C.G. and Le Fevre L.J.W., *J. Chem Soc*., **12**, 4041 (1953).
23. Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Zakrzewski V.G., Montgomery J.A., Stratmann R.E., Burant J.C., Dapprich S., Millam J.M., Daniels A.D., Kudin K.N., Strain M.C., Farkas O., Tomasi J., Barone V., Cossi M., Cammi R., Mennucci B., Pomelli C., Adamo C., Clifford S., Ochterski J., Petersson G.A., Ayala P.J., Cui Q., Morokuma K., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Cioslowski J., Ortiz J.V., Baboul A.G., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Gomperts R., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Gonzalez C., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Andres J.L., Gonzalez C., Head-Gordon M., Replogle and Pople J.A., Gaussian, Inc., Pittsburgh PA, 1998.
24. Cheryukanova G.Ya., Vulfson S.G., Chmutova G.A. and Vereschagin A.N., *Izv. AN SSSR, ser. khim.*, **11**, 1800 (1974).
25. Freimanis J.F., Dregeris J.J., Berzina L.E., Turovsky I.V., Bitte S.J., Blinov L.M. and Rumyantsev G.V., *Adv. Mol. Relax. Proc*., **5**, 33 (1973).
26. Zhdanov Yu.A. and Minkin V.I., Correlative Analysis in Organic Chemistry, Rostov University, Rostov,1966 (in Rusian).
27. Prezhdo.V.V., Vaschenko E.V., Prezhdo O.V. and Puszko A, *J. Mol. Str*., **510**, 69 (1999).
28. Prezhdo V.V., Bocharova V.V. and Lutskii A.E., *Zh. Obsch. Khim.*, **52**, 2108 (1982).