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Charge-Transfer Complexes between Substituted Pyridine *N*-Oxides and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

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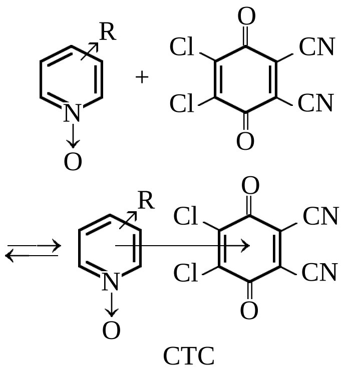
Abstract — Spectrophotometry was used to study charge-transfer complexes between substituted pyridine *N*-oxides and 2,3-dichloro-5,6-dicyano-1,4- benzoquinone. Vertical ionization potentials of pyridine *N*-oxides in the gas phase and in solution were calculated by the CNDO/S3' method. The calculated ionization potentials in chloroform nicely correlate with the experimental charge-transfer wavelengths of the complexes.

It is known that aromatic *N*-oxides can act as donors in donor–acceptor interactions, giving charge-transfer complexes (CTC) with strong π-acceptors. Such complexes are sometimes formed as reaction intermediates [1, 2].

The aim of the present work was to compare some parameters of heteroaromatic *N*-oxides, obtained by studying donor–accepor interactions of these compounds with tetrasubstituted benzoquinones by spectral methods, as well as by quantum-chemical calculations.

The formation of charge-transfer complexes between substituted heteroaromatic *N*-oxides and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in chloroform is readily detected by the appearance of a new long-wave band in the electronic absorption spectrum. The position of this charge-transfer band is determined by the electron affinity of the acceptor and the ionization potential of the donor.



The stability constants of the complexes (K) and their absorption wavelengths were determined by the Benesi–Hildebrand method and are listed in Table 1.

We found a linear dependence (1) between $\log K$ and Brown electrophilic constants of substituents in pyridine *N*-oxides (Fig. 1).

$$\log K = \log K_0 + \rho\sigma. \qquad (1)$$

Here K_0 is the constant of complex formation between unsubstituted pyridine *N*-oxide and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, $\rho = -0.83 \pm 0.06$ is the reaction constant, and σ is the Brown constant. Note that the observation of a dependence like (1) is unequivocal evidence for charge-transfer complex formation [4].

As would be expected, the stability of the complexes markedly decreases in going from *N*-oxides with electron-donor substituents to *N*-oxides with electron-acceptor substituents. According to [5], nitro-substituted *N*-oxides fail to enter complex formation. However, we found that 4-nitropyridine *N*-oxide still forms a charge-transfer complex. The logarithm of the stability constant of this complex fits linear dependence (1) (Fig. 1). The charge-transfer band of the complex of 2,3-dichloro-5,6-dicyano-1,4-benzoqui-

Table 1. Brown constants of substituents in pyridine *N*-oxides (σ), charge-transfer wavelengths (λ_{max}), and stability constants (K) of complexes with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

Substituent	σ [3]	λ_{max}, nm	K	$\log K$
4-NO_2	0.790	421	4.6	0.66
4-Cl	0.114	482	17.3	1.24
H	0	469	22.3	1.35
3-Me	–0.066	476	26.0	1.41
4-Me	–0.311	492	50.6	1.70
4-MeO	–0.778	513	85.1	1.93

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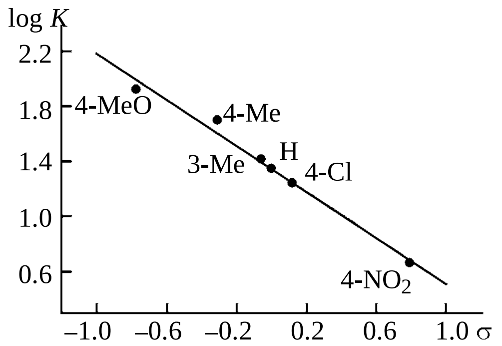

Fig. 1. Plot of the logarithm of the constant of charge-transfer complex formation (log*K*) between substituted pyridine *N*-oxides and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone vs. Brown substituent constants (σ).

none with 4-nitropyridine *N*-oxide is shifted blue and appears as a shoulder on the intrinsic *N*-oxide absorption band. For this reason, the λ_{max} and extinction coefficient of the complex are difficult to determine exactly, but its stability constant could be determined fairly accurately.

We performed quantum-chemical calculations of the ionization potentials of the donors (D) in solution (I_s) and the electron affinities of the acceptor (A) in solution (E_s). These values are related to the charge-transfer energy [$h\nu_{CT}$(DA)] by Eq. (2).

$$h\nu_{CT}(DA) = I_s - E_s - \gamma_s(\varepsilon_\infty, l_{DA}). \qquad (2)$$

Here $\gamma_s(\varepsilon_\infty, l_{DA})$ is a parameter depending on the properties of the donor and acceptor, high-frequency dielectric constant of the solvent (ε_∞), and distance between the donor and acceptor in the complex (l_{DA}).

The quantum-chemical calculations were performed in two steps. The first involved *ab initio* geometry optimization of pyridine *N*-oxides at the RHF level with the STO-4G (STO-4G* for 4-chloropyridine pyridine *N*-oxide) using the GAMESS program [6]. This method provides a good fit of calculation to experiment: We reproduced the experimental N→O and C≡N distances not worse than Makowski *et al.* [7] with the 6-31G and 6-31G* split-valence basis sets. The calculation results are presented in Table 2. In Table 3 we give more detailed data on the equilibrium geometry and dipole moments of 4-chloropyridine *N*-oxide which has been less studied theoretically.

In the second step we calculated the vertical ionization potentials of substituted heteroaromatic *N*-oxides in the gas phase (I_g) and in chloroform (I_s), as well as their dipole moments by the semiempirical CNDO/S3' method [8–11]. The solvent was simulated as a continuum with a dielectric constant and refractive index corresponding to chloroform [12]. Each molecule was placed into a nonspherical cavity formed by intersecting atomic spheres. The radii of the spheres were set equal to van der Waals radii [13] (Å): C 1.7 (three-coordinate atom) and 2.0 (four-coordinate atom), H 1.2, N 1.5, O 1.4, and Cl 1.9. Interatomic electron exchange inside the cavity and dispersion effects associated with fluctuations of atomic charges were taken into account [10, 14].

Table 2. Geometric parameters of pyridine *N*-oxide and its derivatives

Basis	Bond length, Å		CNC angle, deg
	N–O	C–N	
	Pyridine *N*-oxide		
STO-4G	1.32	1.39	117.6
6-31G* [7]	1.28	1.34	120.3
Experiment [7]	1.29	1.38	120.9
	4-Nitropyridine *N*-oxide		
STO-4G	1.31	1.40	121.3
6-31G* [7]	1.25	1.35	119.8
Experiment [7]	1.30	1.37	125.6
	4-Methylpyridine *N*-oxide		
STO-4G	1.33	1.39	117.1
6-31G* [7]	1.28	1.34	119.0
Experiment [7]	1.41	1.43	125.6
	4-Metoxypyridine *N*-oxide		
STO-4G	1.34	1.38	118.2
6-31G* [7]	1.29	1.33	118.9

Table 3. Geometric parameters of 4-chloropyridine *N*-oxide

Basis	Bond length, Å			CNC angle, deg	μ, D
	N–O	C–N	C–Cl		
STO-4G	1.320	1.393	1.754	118.1	1.37
STO-4G*	1.322	1.392	1.703	117.9	2.03
6-31G	1.359	1.337	1.793	123.9	3.78
6-31G*	1.274	1.340	1.732	122.1	3.37
6-31+G*	1.274	1.340	1.732	122.2	3.37

The ionization potential in the gas phase and in solution can be determined by the energy of the highest occupied level, corrected for electron relaxation. In [8–11], the correction was set equal to –0.80 eV. The resulting data are listed in Table 4.

The difference between the gas-phase and solution ionization potentials (ΔI) was calculated by Eq. (3).

Table 4. Ionization potentials (I) and dipole moments (μ) of pyridine N-oxide derivatives and charge-transfer energies of their complexes with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone ($h\nu_{CT}$)[a]

Substituent	$h\nu_{CT}$, eV	I_g, eV	I_s, eV	ΔI, eV	μ_c, D	μ_e, D [14]
4-NO_2	2.94	9.10	8.01	1.09	1.08	0.69
H	2.64	8.57	7.79	0.78	4.15	4.18
3-Me	2.60	8.47	7.72	0.75	4.65	4.33
4-Cl	2.58	8.61	7.67	0.94	2.68	2.82
4-Me	2.51	8.36	7.60	0.76	5.03	4.74
4-MeO	2.42	8.31	7.46	0.85	4.77	5.08

[a] I_g and I_s are the ionization potentials in the gas phase and in solution, respectively; and μ_c and μ_e are the calculated and experimental dipole moments, respectively.

$$\Delta I = I_g - I_s. \tag{3}$$

Here I_g and I_s are the ionization potentials in the gas phase and in solution, respectively.

The solvent effect should be taken into account because it is rather strong and because the ionization potentials of the donors in the gas phase not always vary in parallel with those in solution (see the ionization potential of 4-chloropyridine N-oxide in Table 4).

Note that the calculated dipole moments of heteroaromatic N-oxides nicely fit experimental. These values allow one to judge about the strength of eletrostatic interactions of a neutral molecule of the solvent. The large ΔI corrections for nitro- and chlorine-substituted pyridine N-oxides, whose inclusion changes the order of ionization potentials in chloroform compared with that in the gas phase, is apparently explained by low dipole moments and, as a consequence, a weak solvation stabilization of these compounds before ionization.

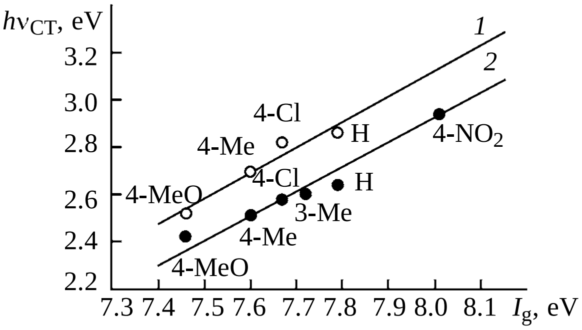

Fig. 2. Plot of the charge-transfer energy ($h\nu_{CT}$) vs. calculated ionization potentials of the donors (I_s) in chloroform for complexes with different acceptors. Acceptor: (*1*) Tetracyanoethylene and (*2*) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetracyanoethylene.

Table 5. Electron-acceptor characteristics of 1,4-benzoquinone (BQ), tetracyanoethylene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (eV)[a]

Acceptor	E_g^e [15]	E_g^c	E_s^c	ΔE
BQ	1.91	1.92	3.20	1.28
TCNE	2.90	2.86	3.70	0.84
DDQ	3.00	2.96	3.86	0.90
TCNQ	2.88	3.11	3.89	0.78

[a] E_g^e, E_g^c, and E_s^c are the electron affinities of the acceptors (experimental in the gas phase and calculated in the gas phase and in solution, respectively); and ΔE is the difference between the calculated electron affinities of the acceptors in the gas phase and in solution.

The same approach is suitable for strong electron acceptors. Table 5 lists the energies of the lowest unoccupied levels for 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 1,4-benzoquinone, tetracyanoethylene, and 7,7,8,8-tetracyanoquinodimethane, calculated by the CNDO/S3' method, as well as the “vertical” electron affinities of these molecules in the gas phase and in chloroform. The equilibrium geometries of the acceptors were calculated *ab initio* at the RHF level with the STO-4G (STO-4G* for 2,3-dichloro-5,6-dicyano-1,4-benzoquinone) basis set.

Figure 2 depicts dependences (4) and (5) of the charge-transfer energies in the complexes of aromatic N-oxides with the 2,3-dichloro-5,6-dicyano-1,4-acceptors on the calculated ionization potentials of the donors in chloroform.

$$h\nu_{CT}(\text{DDQ}) = I_s - E_s(\text{DDQ}) - 1.57,\ \text{eV}, \tag{4}$$

$$h\nu_{CT}(\text{TCNE}) = I_s - E_s(\text{TCNE}) - 1.82,\ \text{eV}. \tag{5}$$

The $h\nu_{CT}$(TCNE) values for the complexes of substituted pyridine N-oxides with tetracyanoethylene were taken from [16].

A unit coefficient at I_s corresponds to full charge transfer on excitation of the complex. The fact that the point for the complex of 4-methoxypyridine with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone deviates from the linear dependence can be explained by the steric features of the methoxy group, which prevents the donor and acceptor molecules from approaching each other at a distance as short as in the other donor–

acceptor pairs. The donor–acceptor distance in the complex of unsubstituted pyridine *N*-oxide should be the shortest, which may explain the deviation of the corresponding point from the linear dependence in the opposite direction.

4-Nitropyridine *N*-oxide has a relatively low dipole moment, and it can be assigned an apparent Born radius in chloroform [Eq. (6)].

$$r_D = 7.2(1 - 1/\varepsilon_\infty)/\Delta I. \quad (6)$$

The radius of an acceptor (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) is determined by Eq. (7).

$$r_A = 7.2(1 - 1/\varepsilon_\infty)/\Delta E. \quad (7)$$

The radii calculated with the data in Tables 4 and 5 (r_D 3.44 and r_A 4.17 Å) we used for estimating l_{DA} for the donor–acceptor complexes. Extending the formalism of Semenov [17], developed for a system of interacting atoms, to a system of two molecules D and A with definite (but changing under photoexcitation) charges, we approximated the last term in Eq. (2) by Eq. (8) (in au) from which we obtained Eq. (9).

$$\gamma_s = (l_{DA}^2 + r_D r_A)^{-1/2}/\varepsilon_\infty, \quad (8)$$

$$l_{DA} = [(14.4/(I_s - E_s - h\nu_{CT})\varepsilon_\infty)^2 - r_D r_A]^{1/2}. \quad (9)$$

In Eq. (9), energies are in eV and radii and distances are in Å.

The resulting charge-transfer distance l_{DA} for the complex of 4-nitropyridine *N*-oxide with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in chloroform (4.25 Å) is larger than the possible donor–acceptor interplanar spacing of 3.4±0.1 Å. This fact implies that the projections of the electron-donor and electron-acceptor centers in a hypothetical donor–acceptor “sandwich” do not coincide at the instant of charge transfer but are drawn by 2.5 Å into the donor or acceptor plane. Such estimates are not accurate enough for more definite conclusions as to the structure of the complexes.

Whether the 2,3-dichloro-5,6-dicyano-1,4-benzoquinone charge-transfer complexes are susceptible to further chemical transformations depends on the ionization potential of the donor. The rate of such a transformation can be followed by the decrease in the optical density at λ_{max} with time. Thus, the complexes with electron-acceptor substituents in the donor component are stable by virtue of the high ionization potentials, whereas the charge-transfer complexes with pyridine *N*-oxides with low I_s values undergo profound transformations. The stability boundary of the complexes of substituted pyridine *N*-oxides with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in chloroform is near the ionization potential of the donor of 7.60 eV. Complexes with donors with higher ionization potentials are stable. The fastest transforming is the complex of 4-metoxypyridine *N*- oxide with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

EXPERIMENTAL

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone and substituted pyridine *N*-oxides were synthesized as described in [18]. Chloroform was purified and dried by known procedures. The electronic absorption spectra were measured on a Specord M-40 spectrophotometer in quartz cells.

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