Aromatic Character of Anthraquinone Derivatives

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The dependence of quinoid C—O distances on π-electron delocalization in anthraquinone ring was investigated. The results obtained by quantum-chemical calculations of model compounds and by statistical processing of 70 data of 29 crystal structures are in very good agreement. The linear functions represent the sufficient approximation of the above dependence.

The molecular structure of hydroxyanthraquinone cannot be expressed in a satisfactory way by a single canonical formula, consequently, two forms *I* and *II* should contribute to the electronic configuration of the molecule.
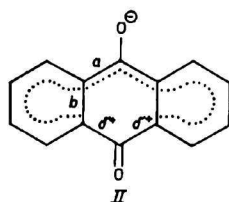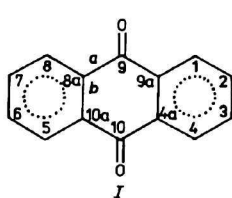
Form *I* corresponds to the quinoid structure normally encountered in anthraquinone derivatives while form *II* represents an extension of π-electron delocalization from the benzene rings to the corresponding C—C—C bridge resulting in a shifting of one half of the central ring from a quinoid to a benzoid structure. The zwitterionic structure *II* implies an anionic character for O-9 whereas the positive charge is delocalized in the cyclic anthraquinone framework. Thus electron transfer from the C-9=O bond to O-9 is accompanied by a change in hybridization of O-9 from sp^2 to sp^3. The longer C—O distances correspond to weaker C—O bonds.

Systematic study of hydroxyanthraquinones [1, 2] discovered a correlation between the π-electron delocalization in hydroxyanthraquinone ring and quinoid C—O distances.

Two relevant C—C bond-length averages in the central ring were denoted by *a* and *b* (see formulae *I* and *II*) and $\Delta = a - b$ was defined. An estimation of bond order of the formal double bond C-9=O and hence the significance of *I* and *II* cannot be made simply from consideration of the C-9—O bond length as the C_{arom}—O⁻ distance tends to be highly sensitive to a partial charge on the aromatic carbon. Nevertheless, from a comparison of bond lengths of a series of compounds, a good correlation between Δ and the C-9—O bond length was found [1, 2]. Obviously, there exists a relationship between the shortening of C—OH bond length and ionization state of oxygen. The bond length becomes shorter if the hydroxyl participates in hydrogen bridge bonding and is intermediate between C—O⁻ and C—OH of nonhydrogen-bonded OH groups.

EXPERIMENTAL

It may be supposed that the correlation found by *Ulický* [1, 2] is not restricted only to the hydroxy derivatives of anthraquinones and, moreover, it could be applied to both quinoid oxygens, too. This assertion can be verified, in principle, in two ways: by theoretical quantum-chemical studies of model compounds and by statistical evaluation of experimental crystallographic data on all the relevant compounds.

The direct connection of these treatments may be implied by the weakening of the C—O bond during its elongation and *vice versa*.

DISCUSSION

Quantum-Chemical Studies

The dependence of C—O bond order and corresponding charge of O atom on the geometry of the central ring in the anthraquinone derivatives may be studied by quantum chemistry methods on model systems.

For the sake of simplicity, let us suppose that only the geometry of the central ring is changed (thus b = const.) and the mirror plane passing through both C—O groups is conserved (C_{2v} symmetry). Under these conditions, the changes of the Δ parameter may be described as a superposition of the following independent deformation modes:

– stretching of all C—C bonds corresponding to the a parameter (C-9—C-8a, C-9—C-9a, C-10—C-10a, and C-10—C-4a), all angles are constant (model a),

– varying of angles at carbons in *ortho*-position (C-9—C-8a—C-10a and C-9—C-9a—C-4a) with the constant ones in *meta*- (C-8a—C-10a—C-10 and C-9a—C-4a—C-10) and *para*-positions (C-4a—C-10—C-10a) to the relevant C—O group (model o),

– varying of angles at carbons in *meta*-position (C-8a—C-10a—C-10 and C-9a—C-4a—C-10) with the constant ones in *ortho*- (C-9—C-8a—C-10a and C-9—C-9a—C-4a) and *para*-positions (C-4a—C-10—C-10a) to the relevant C—O group (model m),

– varying of angles at carbons in *para*-position (C-4a—C-10—C-10a) with the constant ones in *ortho*- (C-9—C-8a—C-10a and C-9—C-9a—C-4a) and *meta*-positions (C-8a—C-10a—C-10 and C-9a—C-4a—C-10) to the relevant C—O group (model p).

Using standard semiempirical INDO method [3, 4] the model compounds 9,10-anthracenedione (A), 1,8-dihydroxy-9,10-anthracenedione (DA), 1,3,6,8-tetrahydroxy-9,10-anthracenedione (TA) are studied. Their idealized geometries (Table 1) are varied according to the above-mentioned deformation models. For such geometrical configurations

the calculated values of oxygen net charges Q and Wiberg (bond strength) indices W of the C—O bond may be approximated as

$$Q - Q_{ref} = k_Q \Delta \qquad (1)$$

$$W - W_{ref} = k_W \Delta \qquad (2)$$

where Q_{ref} and W_{ref} are oxygen charges and Wiberg (bond strength) indices of the reference geometry, respectively, k_Q and k_W are the proportionality constants evaluated by the least-squares method, respectively.

The results obtained by linear regression analysis of INDO calculations are collected in Table 2. Their reliability may be assessed *via* statistical characteristics such as standard deviations (in parentheses) and the correlation coefficients.

Statistical Studies

This part is concentrated on the systematic study of the correlation of the dependence of Δ *vs.* C—O distances in all anthraquinone derivatives. The interatomic distances were obtained from the Cambridge Structural Database [5]. The structures with crystallographic R-value over 0.06 were excluded from our consideration in order to minimize the experimental errors. Under these conditions 29 compounds (Table 3) were selected. The values of a and b corresponding to the same quinoid oxygen were averaged. Consequently, 70 data on Δ and C—O distances were considered (some compounds contain more anthraquinone fragments).

The obtained correlation of Δ *vs.* C—O distances shown in Fig. 1 is linear and it may be described by the equation

$$d(C—O) = -1.194\ \Delta + 1.317 \qquad (3)$$

with the correlation coefficient of 0.9337.

Table 1. Reference Geometries of A, DA, and TA Compounds

Interatomic distances/Å		Valence angles/°	
C—C	1.39	C—C—C	120
C=O	1.21	C—C—O	120
C—OH	1.40	C—C—H	120
C—H	1.10	C—O—H	109
O—H	0.90		

Table 2. Calculated Parameters of A, DA, and TA Compounds

Compound	A				DA				TA			
Model	a	o	m	p	a	o	m	p	a	o	m	p
Number of configurations	9	8	13	7	9	9	13	7	9	9	13	7
Δ_{min}/Å	−0.04	−0.02	−0.04	−0.08	−0.04	−0.02	−0.04	−0.08	−0.04	−0.02	−0.04	−0.08
Δ_{max}/Å	0.12	0.06	0.09	0.17	0.12	0.06	0.09	0.17	0.12	0.06	0.09	0.17
k_Q/(e Å^{-1})	0.248(3)	0.321(5)	0.22(1)	0.265(8)	0.209(2)	0.267(3)	0.159(2)	0.25(1)	0.196(2)	0.266(3)	0.133(7)	0.233(7)
Correlation coefficient of eqn (1)	0.9992	0.9992	0.9972	0.9977	0.9997	0.9993	0.9985	0.9974	0.9995	0.9994	0.9780	0.9975
k_W/Å^{-1}	0.79(1)	0.893(9)	0.93(1)	0.75(2)	0.79(1)	0.88(1)	0.88(1)	0.76(2)	0.78(1)	0.89(1)	0.88(1)	0.75(2)
Correlation coefficient of eqn (2)	0.9989	0.9995	0.9980	0.9977	0.9987	0.9994	0.9990	0.9977	0.9990	0.9993	0.9991	0.9975

Table 3. Interatomic Distances (d/Å)

Compound	R-value	C-9—C-8a C-10a—C-10	C-9—C-9a C-10—C-4a	C-4a—C-9a	C-8a—C-10a	C-9—O C-10—O	Ref.
γ-Rhodomycinone	0.047	1.413	1.395	1.428	1.382	1.350	[6]
		1.415	1.406			1.349	
		1.485	1.444	1.428	1.425	1.255	
		1.474	1.445			1.258	
		1.462	1.451	1.435	1.417	1.259	
		1.482	1.457			1.255	
		1.430	1.395	1.435	1.386	1.342	
		1.418	1.388			1.310	
Versicolorin C	0.053	1.492	1.470	1.421	1.420	1.230	[7]
		1.440	1.459			1.266	
Pyridinium 1-amino-4-bromo-anthraquinone-2-sulfonate	0.033	1.510	1.473	1.378	1.430	1.215	[8]
		1.471	1.482			1.229	
7,8-Dihydro-1,6-dimethoxy-naphthacene-5,10,12(9H)-trione	0.051	1.473	1.500	1.413	1.412	1.215	[9]
		1.481	1.502			1.209	
6,13-Pentacenedione	0.041	1.488	1.483	1.428	1.428	1.215	[10]
		1.483	1.488			1.215	
Alizarin-9-dicyanomethylene-2,4,7-trinitrofluorenone acetonitrile	0.046	1.457	1.478	1.436	1.401	1.260	[11]
		1.481	1.462			1.230	
1,4-Dihydroxyanthraquinone	0.036	1.476	1.457	1.424	1.396	1.236	[12]
		1.471	1.457			1.237	
1,4-Bis(isopropylamino)anthraquinone	0.056	1.496	1.464	1.440	1.390	1.256	[13]
		1.480	1.461			1.260	
Benz[a]anthracene-7,12-dione	0.045	1.480	1.470	1.382	1.386	1.226	[14]
		1.486	1.508			1.213	
[2.0.0](1,4)Benzeno(1,8)anthraquinono-(1,4)-benzenophane	0.055	1.492	1.493	1.393	1.396	1.220	[15]
		1.489	1.488			1.214	
1,8-Dinitro-4,5-dihydroxyanthraquinone	0.044	1.491	1.490	1.397	1.404	1.218	[16]
		1.462	1.459			1.242	
1-[2-(Diethylamino)ethylamino]-9,10-anthracenedione	0.049	1.489	1.463	1.407	1.401	1.238	[17]
		1.469	1.497			1.225	
1,4-Bis(butylamino)anthraquinone	0.050	1.480	1.437	1.448	1.402	1.254	[18]
		1.469	1.449			1.255	
2-(2-Hydroxy-2-methyl-3-oxobutyl)-3-methylnaphtho[2,3-f]quinoxaline-7,12-dione	0.039	1.499	1.468	1.396	1.395	1.224	[19]
		1.492	1.494			1.220	
		1.491	1.469	1.397	1.395	1.225	
		1.491	1.494			1.221	
1-[(4-(Dimethylamino)phenyl)amino]-4-hydroxy-9,10-anthracenedione	0.044	1.459	1.467	1.391	1.437	1.251	[20]
		1.441	1.487			1.243	
1,4,7,22,25,28-Hexaoxa[7.7](9,10)-anthracenophane	0.056	1.386	1.398	1.444	1.442	1.380	[21]
		1.405	1.387			1.394	
		1.394	1.375	1.430	1.442	1.391	
		1.381	1.394			1.387	
1,4,7,10,25,28,31,34-Octaoxa[10.10](9,10)-anthracenophane	0.031	1.404	1.387	1.430	1.434	1.390	[21]
		1.391	1.402			1.386	
1-[(4-(Dimethylamino)phenyl)amino]-9,10-anthracenedione	0.053	1.489	1.471	1.403	1.418	1.225	[22]
		1.458	1.492			1.231	
2',2'-Dimethyl-5,10-dioxoanthra[1,2-e]-(1',4',2')dioxasilane	0.052	1.480	1.482	1.380	1.416	1.232	[23]
		1.484	1.482			1.201	
2',2'-Dimethyl-5,10-dioxoanthra[1,2-e]-(10,4',2')dioxasilane	0.039	1.464	1.490	1.375	1.420	1.230	[23]
		1.498	1.495			1.211	
1-Acetyl-2,4,5,7-tetrahydroxy-9,10-anthracenedione	0.052	1.445	1.429	1.435	1.427	1.270	[1]
		1.487	1.485			1.216	
catena-(Bis(di-μ-perchlorato-O,O')-1,4,7,10,13,28,31,34,37,40-decaoxa[13.13](9,10)-anthracenophane sodium)	0.052	1.381	1.388	1.441	1.434	1.407	[24]
		1.382	1.376			1.415	
Diaqua-(7-β-D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarboxylate-O,O',O'',O''') potassium monohydrate	0.041	1.485	1.458	1.426	1.430	1.246	[25]
		1.484	1.444			1.238	
		1.444	1.484	1.430	1.426	1.238	
		1.458	1.485			1.246	
1-Amino-4-phenylamino-9,10-anthracenedione	0.050	1.459	1.486	1.391	1.441	1.247	[26]
		1.452	1.479			1.242	
N-(9,10-Dihydro-9,10-dioxo-1-anthryl)-3-[4-(3-hydroxypropyl)piperazin-1-yl]-propanamide	0.044	1.483	1.489	1.409	1.387	1.222	[27]
		1.489	1.479			1.219	
1,4-Diaminoanthraquinone dihydrate	0.039	1.479	1.440	1.445	1.398	1.254	[28]
		1.479	1.440			1.254	
1,4-Dihydroxy-2-(1-hydroxy-2,3:4,5-di-O-isopropylidene-D-arabinityl)anthraquinone	0.027	1.481	1.461	1.418	1.385	1.234	[29]
		1.482	1.456			1.251	
6,16-Dihexyldinaphtho[1,2-a:1',2'-h]-9,18-anthracenedione	0.034	1.503	1.483	1.376	1.376	1.217	[30]
		1.483	1.503			1.217	
7-Methoxy-2-methyl-4,5-dihydroxy-9,10-anthracenedione	0.059	1.478	1.516	1.403	1.404	1.226	[2]
		1.461	1.459			1.274	

a and b are defined as $a = [d(\text{C-9—C-8a}) + d(\text{C-9—C-9a})]/2$ and $a = [d(\text{C-10a—C-10}) + d(\text{C-10—C-4a})]/2$, respectively, $b = [d(\text{C-4a—C-9a}) + d(\text{C-8a—C-10a})]/2$.
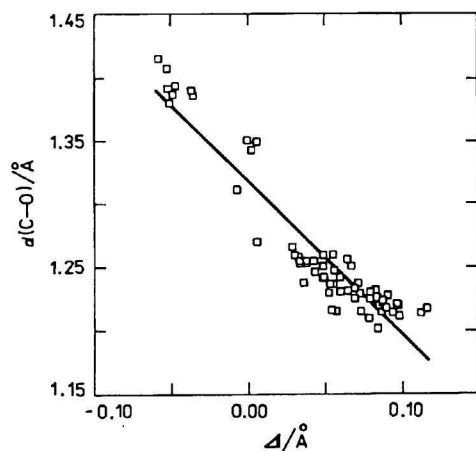
Fig. 1. The experimental correlation of the dependence of Δ vs. C—O distances.

CONCLUSION

The results of quantum-chemical studies may be summarized as follows:

High values of all the correlation coefficients indicate that the used linear functions represent very good approximation within the conformations under study. The positive values of k_Q and k_W constants imply the lowering of negative oxygen charges and the increasing of C—O bond strength (and thus its shortening in real systems) with increasing Δ value. It supports the assertion that the portion of quinoid structure *I* in real systems increases with Δ value and *vice versa*.

Moreover, the k_Q values indicate the highest sensitivity of the oxygen charges to the deformation in *ortho*-position whereas those ones in *meta*-positions exhibit the lowest sensitivity. On the other hand, the influence of deformations in *ortho*- and *meta*-positions on the Wiberg index values is equal.

Despite the —OH groups at positions 3 and 6 usually support the influence of —OH groups at positions 1 and 8, our results showed their non-vanishing influence on the k_Q values only.

The results of statistical studies of a great number of experimental data confirmed the above-mentioned theoretical results (despite the geometry of the model systems is not fully optimized). According to the correlation coefficient value, the linear function (3) is a very good approximation of the C—O distance *vs.* Δ dependence. Its slope is negative, *i.e.* the increasing delocalization of π-electrons in the central ring causes the shortening and strengthening of the C—O bond.

The absolute value of Δ represents the magnitude of deviations from the maximal conjugation. The negative Δ values correspond to anthracenophanes where the bivalent O-9 atom is of ether type.

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