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Synthesis and Structure of 2-Aryl-4*H*-acenaphth[5,6-*bc*]oxepin-4-ones

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Abstract—Oxidation of 2-aryl-7,8-dihydro-4*H*-acenaphth[5,6-*bc*]oxepin-4-ones with chloranil led to the formation of 2-aryl-4*H*-acenaphth[5,6-*bc*]oxepin-4-ones. Their spectral characteristics were analyzed, and a calculation of the molecular structure of model and real compounds was carried out.

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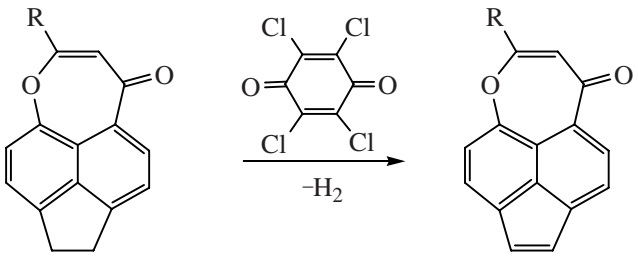
The idea of converting nonaromatic molecules into aromatic by introducing one multiple bond is very attractive since it permits direct contemplation of the changes in the chemical and physical properties during this transformation. Excellent objects of such investigation are peri-fuzed heterocyclic derivatives of acenaphthene and acenaphthylene.

Studies we recently have begun [1] on purposeful carrying out this idea concern in this report the transformation of previously obtained [2] 2-aryl-substituted 7,8-dihydro-4*H*-acenaphth[5,6-*bc*]oxepin-4-ones **Ia** and **Ib** into the corresponding 2-aryl-substituted 4*H*-acenaphth[5,6-*bc*]oxepin-4-ones **IIa** and **IIb**. Compounds **Ia, Ib, IIa**, and **IIb** were studied by IR, ^{1}H NMR, and mass spectroscopy, and also by quantum-chemical calculations of real (R = Ar) and model (R = H) compounds. The experimental and calculated spectral characteristics of aromatic (**IIa** and **IIb**) and nonaromatic molecules (**Ia** and **Ib**) were compared. The conversion of acenaphthene derivatives **I** into acenaphthylene **II** occurs at dehydrogenation of the former with chloranil.



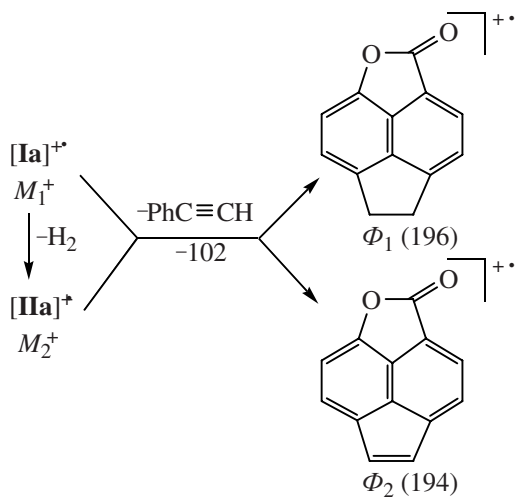
Ia–**Ic** **IIa**–**IIc**

R = Ph (**a**), 4-MeOC$_6$H$_4$ (**b**), H (**c**).

IR spectra of compounds **Ia, IIa** and **Ib, IIb** do not significantly differ in the characteristic region. The carbonyl band of all compounds is located in the region 1630 cm^{-1}, indicating, firstly, that it is influenced only by the heterocyclic part of the molecule, and secondly, the considerable "betainization" of the heteroring.

In the ^{1}H NMR spectra of acenaphthene oxepinones **I** the most upfield signal belongs to the singlet of the proton from the heterocycle (6.34 and 6.30 ppm), and the most downfield doublet signal originates from aromatic proton H^5 (8.44 and 8.38 ppm respectively). The same protons in the spectra of acenaphthylene derivatives **II** appear at 6.7, 6.65 and 6.74, 8.72 ppm respectively. In other words, all spectrum in the region of aromatic protons of acenaphthylene compounds **II** is shifted downfield by 0.3–0.4 ppmcompared with acenaphthene derivatives **I** which may be regarded as an insignificant increase in the aromaticity of the former. The double bond protons arising from dehydrogenation of the bimethylene unit also gain an aromatic character and appear as doublets in the ^{1}H NMR spectra of compounds **II** in the range 7.2–7.4 ppm

In the mass spectrum of 2-phenyl-7,8-dihydro-4*H*-acenaphth[5,6-*bc*]oxepin-4-one (**Ia**) an ejection of a hydrogen molecule was observed resulting in transformation of molecular ion M_1^+ (**Ia**) into M_2^+ (**IIa**) and concurrently occurred an elimination of phenylacetylene to form an ion of acenaphtho[1,8-*bc*]furan-2-



one Φ_1. The phenylacetylene elimination takes place also with molecular ion M_2^+ to give 5,6-dehydroacenaphtho-[1,8-*bc*]furan-2-one Φ_2.

Quantum-chemical calculations were performed in order to establish the structural characteristics and electronic structure of the experimentally obtained compounds and their simplified models. The study was carried out in the framework of the density functional theory by the method B3LYP/6-31G** applying software GAUSSIAN 03 [3]. For model compounds **Ic** and **IIc** were also performed additional calculations by the method B3LYP/6-311+G** [2]. The results of the theoretical treatment for various substituents demonstrated that the structural characteristics of systems **I** and **II** in all cases considered were similar and notably differed only in the region of the carbon-carbon bond which changed the multiplicity (Fig. 1–3).

It was also found that all nonhydrogen atoms of model systems **Ic** and **IIc** form a mirror plane (Fig. 3). A similar planar fragment is conserved in all substituted systems at R = Ph, 4-$MeOC_6H_4$ (Fig. 1, 2), therewith the aromatic substituents are outside of the conjugation plane of the system (rotation angle ~30 deg) and are not involved in the formation of the united π-system.

Notwithstanding the similarity of the structural characteristics the distribution of the electron density in

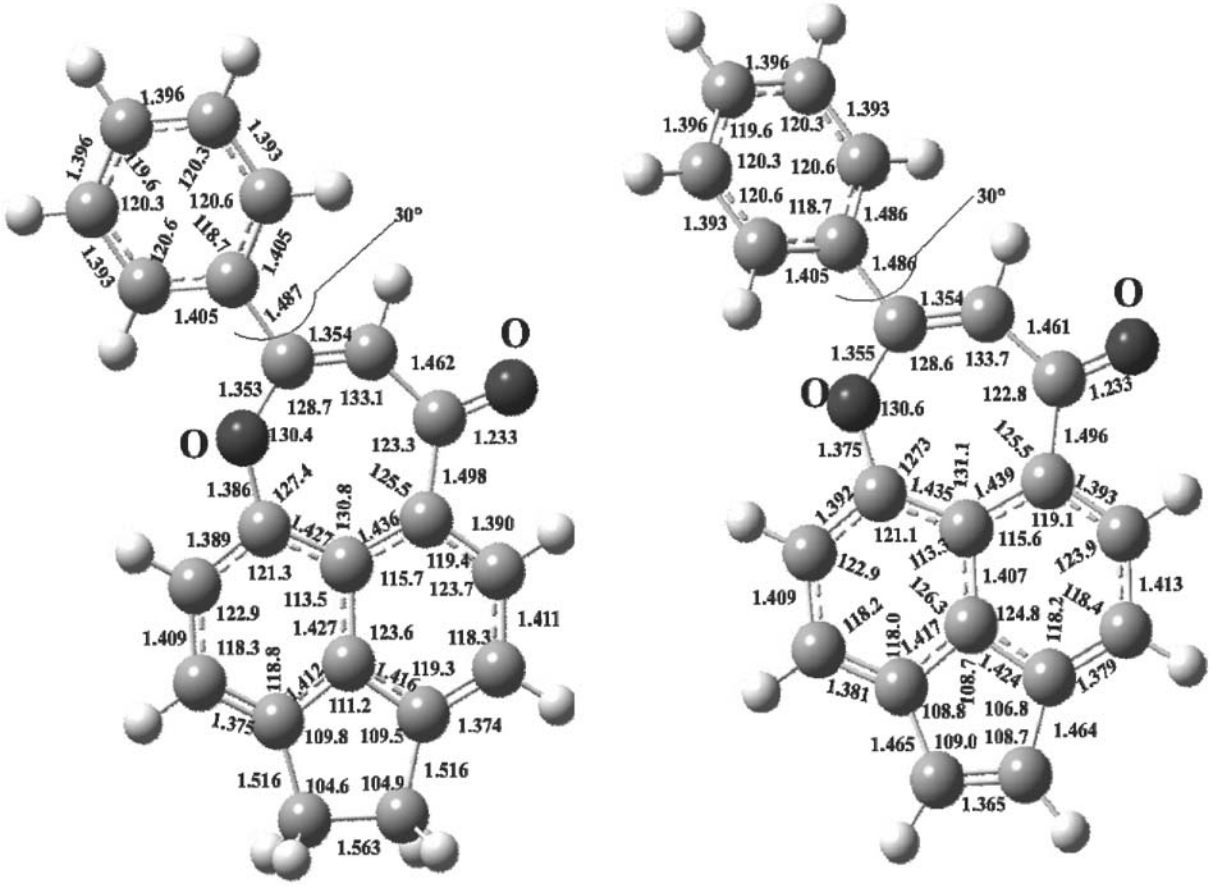


Fig. 1. Geometrical characteristics of structures of 2-phenyl-7,8-dihydro-4*H*-acenaphth[5,6-*bc*]oxepin-4-one (**Ia**) and 2-phenyl-4*H*-acenaphth[5,6-*bc*]oxepin-4-one (**IIa**).

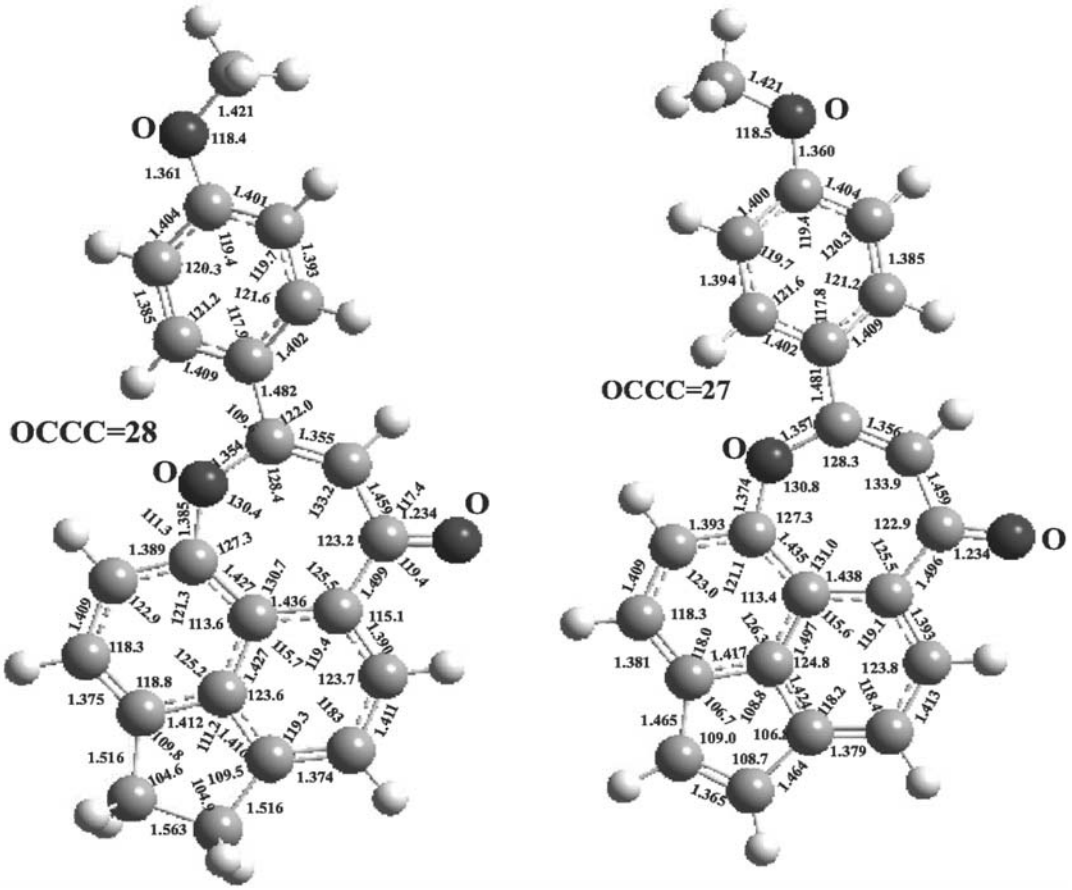


Fig. 2. Geometrical characteristics of structures of 2-(methoxyphenyl)-7,8-dihydro-4*H*-acenaphth[5,6-*bc*]oxepin-4-one (**Ib**) and 2-(methoxyphenyl)-4*H*-acenaphth[5,6-*bc*]oxepin-4-one (**IIb**).

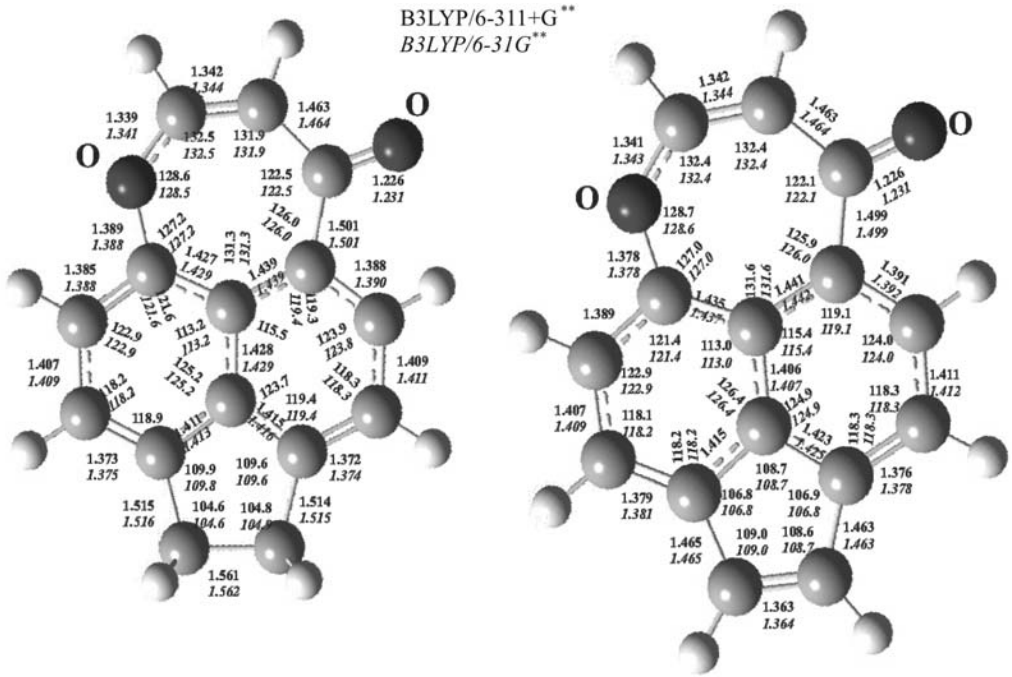


Fig. 3. Geometrical characteristics and charge distribution for the structures of 7,8-dihydro-4*H*-acenaphtho[5,6-*bc*]oxepin-4-one (**Ic**) and 4*H*-acenaphthO[5,6-*bc*]oxepin-4-one (**IIc**).

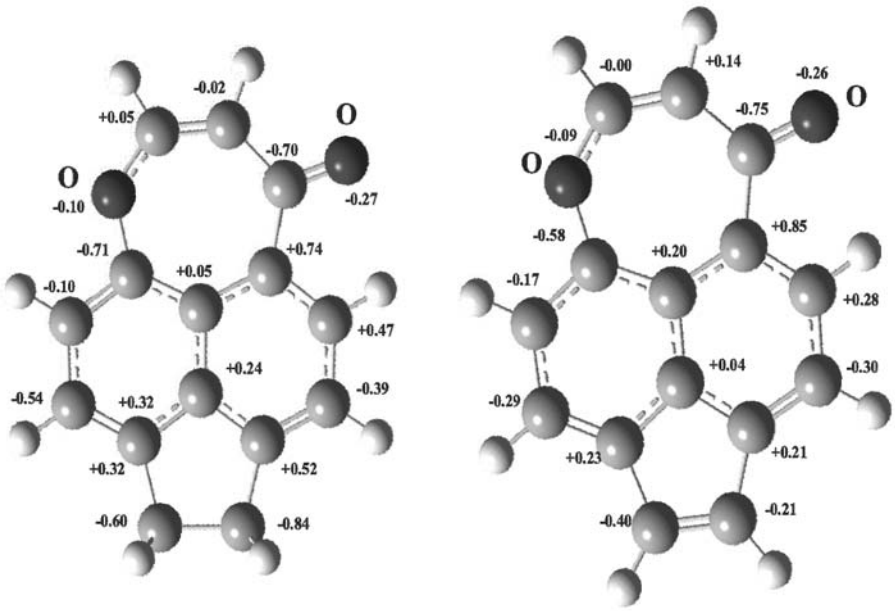


Fig. 4. Charge distribution for the structures 7,8-dihydro-4*H*-acenaphtho[5,6-*bc*]oxepin-4-one (**Ic**) and 4*H*-acenaphtho[5,6-*bc*]oxepin-4-one (**IIc**).

systems **I** and **II** is somewhat different (Fig. 4). For instance, in system **IIc** the electron density is more delocalized as shows, in particular, the lower value of its dipole moment [3.516 D, for compound **Ic** 4.475 D]. This fact may serve an indirect confirmation of the higher aromaticity of systems **II** than **I**.

EXPERIMENTAL

IR spectra of compoumds obtained were recorded on a spectrophotometer Specord 71IR from mulls in mineral oil. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Varian Unity-300 in $CDCl_3$, internal reference HMDS. Mass spectra were measured on a Kratos instrument with a direct admission of a sample into the ion source (ionizing energy 70 eV, control voltage 1.75 kV). The spectra presented below of formerly prepared compounds **Ia** and **Ib** were recorded once more on the same instruments and under the same conditions as the spectra of compounds **IIa** and **IIb**.

2-Phenyl-7,8-dihydro-4*H*-acenaphth[5,6-*bc*]oxepin-4-one (Ia) [2]. IR spectrum, ν, cm^{-1}: 1630, 1607, 1593. ^{1}H NMR spectrum, δ, ppm: 3.45 m (4H, CH_2CH_2), 6.34 s (1H, H^3), 7.28 d (1H, H^{10}, *J* 7.61 Hz), 7.33 d (1H, H^6, *J* 7.41 Hz), 7.37 d (1H, H^9, *J* 7.61 Hz), 7.46–7.52 m (3H, H_{Ph}), 7.87–7.94 m (2H, H_{Ph}), 8.40 d (1H, H^5, *J* 7.44 Hz). Mass spectrum, *m/z* (I_{rel}, %): 298 $[M_1]^+$ (28), 296 $[M_2]^+$ (22), 196 (T_1) (70), 194 (Φ_2) (100), 138 (90).

2-(Methoxyphenyl)-7,8-dihydro-4*H*-acenaphth-[5,6-*bc*]oxepin-4-one (Ib) [2]. IR spectrum, ν, cm^{-1}: 1633, 1607, 1595. ^{1}H NMR spectrum, δ, ppm: 3.40 m (4H, CH_2CH_2), 3.90 s (3H, CH_3O), 6.30 s (1H, H^3), 6.98 d (2H_{arom}, *J* 8.95 Hz), 7.22–7.36 m (3H, H^{6,9,10}), 7.87 d (2H_{arom}, *J* 7.95 Hz), 8.38 d (1H, H^5, *J* 7.40 Hz).

2-Phenyl-4*H*-acenaphth[5,6-*bc*]oxepin-4-one (IIa). A mixture of 0.1 g (0.34 mmol) of compound **Ia** and 0.165 g (0.68 mmol) of tetrachloro-1,4-benzoquinone was boiled for 2 h in 3 ml of *o*-dichlorobenzene. The solution was evaporated to dryness, the residue was subjected to chromatography on aluminum oxide (eluent chloroform). Yield 0.035 g (35%), mp 85–87°C. IR spectrum, ν, cm^{-1}: 1625, 1600, 1580. ^{1}H NMR spectrum, δ, ppm: 6.70 s (1H, H^3), 7.22 d (1H, H^7, *J* 5.24 Hz), 7.37 d (1H, H^8, *J* 5.24 Hz), 7.50 m (3H, H_{Ph}), 7.63 d (1H, H^5, *J* 7.58 Hz), 7.86 d (1H, H^6, *J* 7.58 Hz), 7.96–8.20 m (3H, H^{10} + H_{Ph}), 8.74 d (1H, H^9, *J* 7.36 Hz). Mass spectrum, *m/z* (I_{rel}, %): 296 $[M_2]^+$ (20), 194 (Φ_2) (100), 138 (80). Found, %: C 85.32; H 3.85. $C_{21}H_{12}O_2$. Calculated, %: C 85.14; H 4.05. *M* 296.324.

2-(Methoxyphenyl)-4*H*-acenaphth[5,6-*bc*]oxepin-4-one (IIb) was similarly prepared. Yield 40%, mp 144–147°C. IR spectrum, ν, cm^{-1}: 1625, 1600, 1580. ^{1}H NMR spectrum, δ, ppm: 3.80 s (3H, CH_3O), 6.53 s (1H, H^3), 7.03 d (2H_{arom}, *J* 8.94 Hz), 7.21 d (1H, H^7, *J* 5.24 Hz), 7.35 d (1H, H^8), 7.61 d (1H, H^5, *J* 7.58 Hz), 7.85 d (1H, H^6, *J* 7.54 Hz), 7.96 d (2H_{arom}, *J* 8.94 Hz), 7.98 d (1H, H^{10}, *J* 7.36 Hz), 8.72 d (1H, H^9, *J* 7.36 Hz). Found, %:

C 81.37; H 4.00. $C_{22}H_{14}O_3$. Calculated, %: C 80.98; H 4.29.

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