ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 5, pp. 913–918. © Pleiades Publishing, Ltd., 2008.
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A DFT Study of 2,2'-Bi-1,10-phenanthroline and Its Reduced Form as a Potential Ligand for New Tetraaza Chromophore Complexes

N. S. Panina, V. N. Demidov, and S. A. Simanova

St. Petersburg State Institute of Technology (Technical University),
Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: natali@AP2707.spb.edu

Received October 29, 2007

Abstract—1,10-Phenanthroline, 2,2'-bi-1,10-phenanthroline, and its dianion were examined by DFT B3LYP calculations in the 6-31G** basis set using the GAMESS-2006 program complex. The rigid tetradentate heterocycle, 2,2'-bi-1,10-phenanthroline, in the reduced electron-excessive form L^{2-} creates more favorable geometric and electronic conditions for insertion of complexing ions in its cavity, compared to the neutral ligand.

DOI: 10.1134/S1070363208050137

The precursors of 2,2'-bi-1,10-phenanthroline, 1,10-phenanthroline (1,10-phen) and its monomeric derivatives, are used for a long time as heterocyclic N-donor π-electron-deficient ligands in coordination compounds of the majority of *d* elements [1–4] and of lanthanides [5]. Complexes of this type are actively studied as catalysys [6, 7], biochemical agents and potential drugs [8–13], biochemical nanoprobes [14], DNA intercalators [15–19], and components of supramolecular ensembles [20]. Numerous papers concern complexes of metals with 1,10-phenanthrolines and bi-1,10-phenanthrolines in which 1,10-phenanthroline fragments are linked through spacers [21, 22], as well as the synthesis of macrocyclic 2,9-diaza- or 2,9-dithia-bridged bis-1,1-phenanthrolines [23]. At the same time, studies of coordination compounds with C–C dimers in which the 1,10-phenanthroline fragments are linked not via a bridging group but directly by the interfragment C–C bond are relatively few [24–26]. Of particular interest is the reduced electron-excessive form of such dimeric bi-1,10-phenanthrolines. These species enter as ligands into the composition of novel tetraaza chromophore 1,10-phenanthrocyanine complexes of *d* elements [27–29]. Some of these complexes exhibit redox sensitivity and high affinity for polymeric biological substrates and are of interest as potential biocides. In this connection, a comprehensive chemical and physicochemical study of this class of compounds becomes topical.

This paper deals with a quantum-chemical study of the electronic and geometric structure of 2,2'-bi-1,10-phenanthroline and its electron-excessive reduced derivative, $[2,2'\text{-bi-1,10-phenanthroline}]^{2-}$, and of their complexing power.

The electronic structure of the compounds was calculated by the DFT B3LYP method in the 6-31G** basis set for nontransition element atoms and with the HW pseudopotentials for *d*-element atoms [30], using the GAMESS-2006 program package [31].

2,2'-Bi-1,10-phenanthroline (2,2'-bi-1,10-phen) is a system of two mutually bonded 1,10-phenanthroline fragments. Its properties should be a priori more complex than those of monomeric 1,10-phenanthroline. There are numerous experimental data in the literature on the properties of 1,10-phenanthroline, which makes it possible not only to consistently pass to studying 2,2'-bi-1,10-phenanthroline, but also to check the quality of the quantum-chemical calculations performed.

The results of optimization of the geometric configuration of the 1,10-phenanthroline molecule are given in Fig. 1. Data on the interatomic distances in this compound are consistent with the aromaticity of the two pyridine rings and benzene ring in its molecule.

When considering the IR spectra, we distinguished three groups of the most prominent (strong and

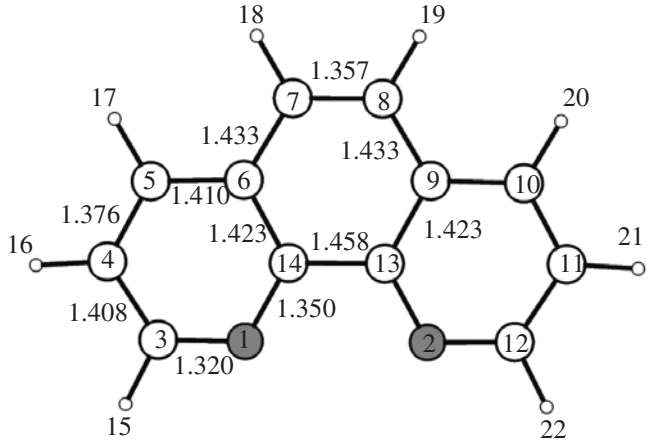


Fig. 1. Geometry of the 1,10-phenanthroline molecule (the interatomic distances are given in Å; the same for Figs. 2 and 3).

medium) bands. In accordance with [32], for 1,10-phen and its substituted derivatives, to these bands belong the vibration bands δ(CH) (about 710–780 cm^{-1}), syn-phase out-of-plane C–H bending vibrations (about 835–855 cm^{-1}), and C=C, C=N stretching vibrations (about 1540–1590 cm^{-1}). The normal mode frequencies of the 1,10-phen molecule, calculated in this study on the basis of DFT force field in the harmonic approximation (see table), are, on the whole, in reasonable agreement with the published experimental [5, 33–35] and theoretical [36] data.

The dipole moment μ of the 1,10-phenanthroline molecule, calculated from the electron density distribution, is 3.8 D (the experimental value is 3.64 D [37]). The nitrogen atoms bear negative charges q_N –0.27 *e*, which makes this molecule attractive from the viewpoint of complexation with metal ions. The low energy of electron removal from the highest occupied molecular orbital (HOMO), equal to 6.49 eV, is also favorable for donor properties of 1,10-phenanthroline.

First, we performed by the method of molecular mechanics the conformational analysis of 2,2'-bi-1,10-phenanthroline. It showed that two structures of 2,2'-bi-1,10-phen are the most probable: planar *cis* conformation (*syn* conformation) and partially unfolded conformation in which the dihedral angle NCCN between the planes of the two 1,10-phenanthroline fragments is equal to 133°, instead of the expected *trans* (*anti*) conformation with the angle of 180°. In the DFT calculation, the partially unfolded conformation of 2,2'-bi-1,10-phen transformed in the course of the geometry optimization into the more stable *trans* form of 2,2'-bi-1,10-phen (Figs. 2a, 2b). This result is consistent with the X-ray structural data recently obtained for 2,2'-bi-1,10-phenanthroline [24]. In the crystal solvate with chloroform, 2,2'-bi-1,10-phen·$CHCl_3$, the 2,2'-bi-1,10-phenanthroline molecules also occur in the *trans* conformation (have transoid geometric structure), similar to that of 2,2'-bipyridine and 2,2':6',2":6",2"'-quaterpyridine, with a small angle [10.0(2)°] between the two planar 1,10-phenanthroline fragments. From the Rice and Anderson's viewpoint [24], this structure ensures optimal π–π interactions. As noted in [24], in the *trans* conformation the interaction between the lone electron pairs of the nitrogen atoms of the two 1,10-phenanthroline fragments linked by the C–C bond is minimal. In contrast to 1,10-phenanthroline and 2,2':6',2":6",2"'-quaterpyridine, in crystals of the solvate 2,2'-bi-1,10-phen·$CHCl_3$ there are no π–π stacking contacts, presumably because of the presence of three chloroform molecules of crystallization in the crystal lattice. Coordination of 2,2'-bi-1,10-phen to Ni^{2+} ions in methanol is accompanied by transition of the *trans* conformation of 2,2'-bi-1,10-phen into the *cis* form with the formation of the mononuclear cation $[Ni(2,2'\text{-bi-1,10-phen})Cl(H_2O)]^+$ in which 2,2'-bi-1,10-phenanthroline, coordinated in the tetradentate fashion, is also almost planar with the angle between the planes of 1,10-phenanthroline fragments equal to 5.6(1)° [24]. This fact suggests that the difference between the energies of the *trans* and *cis* conformers of 2,2'-bi-1,10-phen, $\Delta E_{trans>cis} = E_{cis} - E_{trans}$, it not too large and can be compensated by the complexation energy. Indeed, according to the results of our DFT calculations, the difference between the energies of the conformers ΔE is 51.30 kJ mol^{-1}. This value is within the range typical of common intermolecular interactions in liquid media. Similar pattern is observed with a simpler structural analog of 2,2'-bi-1,10-phenanthroline, 2,2'-bipyridine, which occurs in the *trans* conformation in the gas phase and in crystals and readily transforms into the almost planar *cis* form upon coordination to metal ions [38].

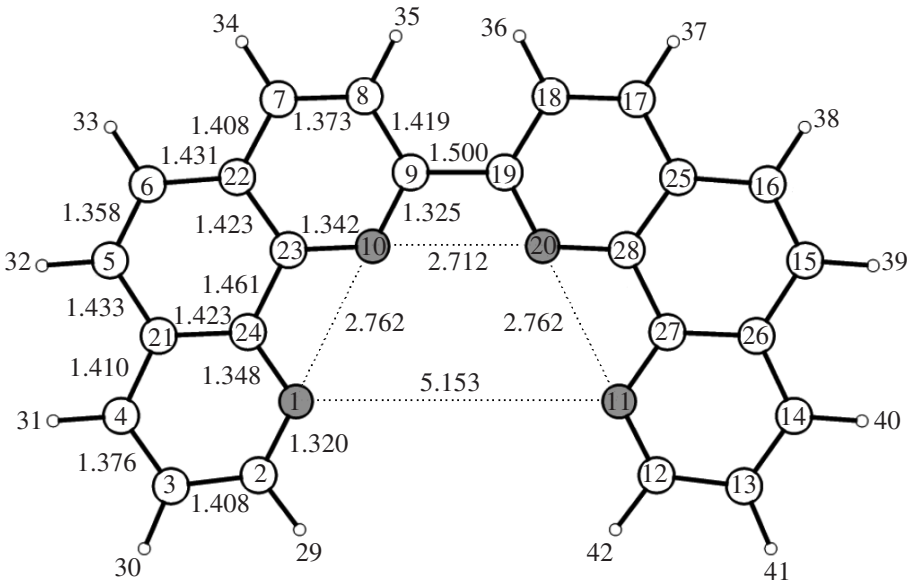
The DFT calculations performed in this study show that the length of the interfragment bond C^9–C^{19} in the *trans*-2,2'-bi-1,10-phen molecule is 1.488 Å, and in the *cis* conformer it is 1.500 Å. The C–C bond lengths in the heteroaromatic pyridine rings are essentially similar in the *trans* and *cis* conformers, namely: 1.408 (C^2–C^3), 1.376 (C^3–C^4), 1.410 (C^4–C^{21}), and 1.423 Å (C^{21}–C^{24}).

Calculated and experimental vibration frequencies of 1,10-phen and *trans*-2,2'-bi-1,10-phen (ν, cm^{-1}; *I,* intensity, D^2/MA^2)

1,10-phen						*trans*-2,2'-bi-1,10-phen
Experiment[a]	Experiment [34]	Experiment [5]	Experiment [35]	Calculation [36]	DFT calculation: ν (*I*)	DFT calculation: ν (*I*)
				600 (0.20)		580 (0.065)
618 m-s	626 s	620 w			631 (0.175)	630 (0.108)
702 m-s				682 (0.07)		643 (0.407)
725 m-s	709			697 (0.17)	714 (0.071)	726 (0.145)
735 v.s	730 s			728 (1.26)	739 (0.102)	730 (0.003)
	738 s	735 s				740 (0.194)
765 m	762	775 s		763 (0.37)	756 (0.815)	758 (0.846)
778 m	772, 776				775 (0.489)	768 (0.039)
815 w	837 s			823 (0.15)	816 (0.001)	774 (0.001)
842 s	845	850 m		836 (1.80)	855 (0.001)	785 (0.710)
852 v.s	852 s			856 (0.15)	858 (1.330)	801 (0.028)
(850 sh)					867 (0.129)	838 (0.361)
880 w						801 (0.028)
	883 s				895 (0.107)	834 (0.361)
						852 (0.069)
						853 (0.010)
965 w				963 (0.01)	961 (0.006)	868 (0.403)
				967 (0.07)	966 (0.005)	877 (2.188)
					980 (0.001)	897 (0.604)
	985			986 (0.01)		898 (0.152)
				988 (0.01)	995 (0.017)	902 (0.011)
						958 (0.014)
						965 (0.004)
						981 (0.012)
						1369 (0.082)
						1411 (0.109)
1420 s	1422 s	1423 s	1406 (20)	1406 (1.42)	1411 (0.001)	1413 (0.001)
		1445 w		1432 (0.09)	1443 (0.001)	1417 (0.719)
		1505 m			1450 (1.172)	1444 (1.196)
	1508		1421 (100)	1475 (0.11)	1478 (0.026)	1472 (1.204)
			1448 (9)	1505 (1.40)	1531 (0.216)	1488 (0.001)
		1558 m				1517 (1.978)
		1584 m	1492 (32)		1536 (0.893)	1533 (0.708)
1540 m	1565		1504 (51)			1534 (0.954)
1590 m	1586			1578 (0.80)	1588 (0.327)	1540 (0.03)
						1578 (1.361)
1618 m	1621		1562 (30)	1602 (0.68)		1625 (0.005)
1635 m			1588 (31)	1616 (0.65)	1630 (0.265)	1629 (1.173)
	1642		1602 (0)		1644 (0.197)	
			1617 (19)			1642 (0.030)
					1656 (0.222)	1645 (1.146)
						1655 (1.202)

[a] For the hydrate 1,10-phen·H_2O in KBr.

(a)



(b)

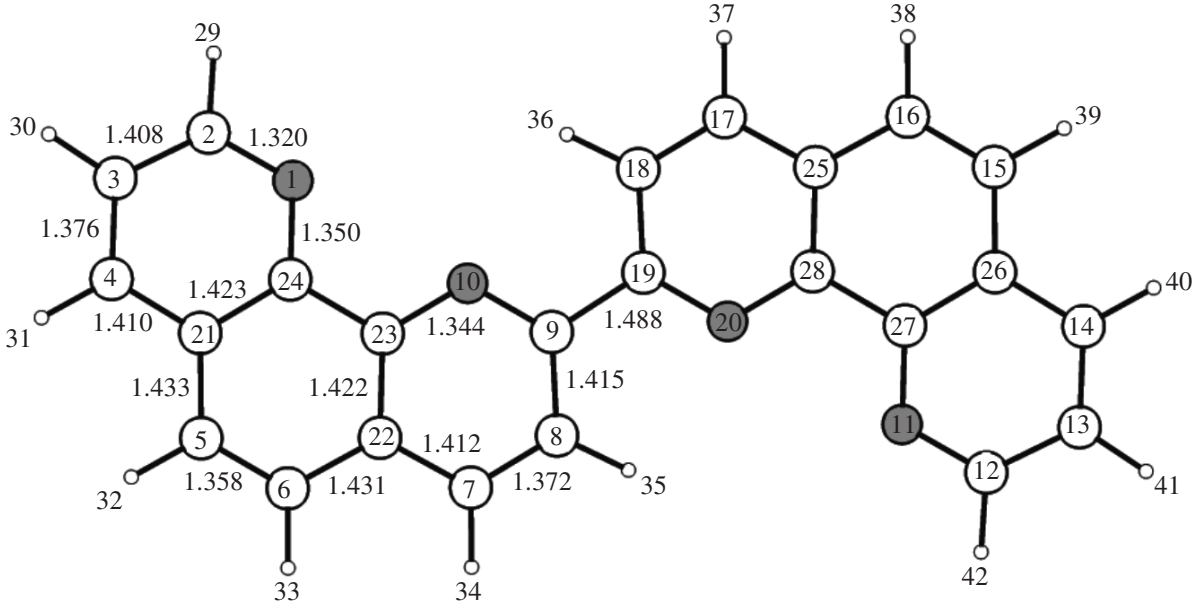


Fig. 2. Geometry of the 2,2'-bi-1,10-phenanthroline molecule: (a) *cis* configuration (with the geometric parameters indicated also for the tetradentate ligand cavity) and (b) *trans* configuration.

The calculated dipole moment μ of the *cis* conformer of the 2,2'-bi-1,10-phenanthroline molecule is 2.7 D, and for the *trans* conformer it is zero. According to the data on the electron density distribution in 2,2'-bi-1,10-phenanthroline, the nitrogen atoms, as in 1,10-phenanthroline, bear negative charges providing the donor power of this ligand in complexation. In the *cis* form, the charges are equal, q_N –0.25 *e*. In the *trans* form, the negative charges are somewhat higher: on the atoms that are the closest to the interfragment bond, $q_{N10} = q_{N20}$ = –0.33 *e*, and on the most remote atoms, $q_{N1} = q_{N11}$ = –0.27 *e*. The energies of electron removal from the HOMO are still lower than in 1,10-phenanthroline: 6.00 (*cis* form) and

6.06 eV (*trans* form), which is also favorable for the donor properties of 2,2'-bi-1,10-phenanthroline.

Owing to the presence of four donor centers, C–C-dimeric 2,2'-bi-1,10-phenanthroline can act as a tetradentate ligand. However, it can fully realize its coordination capacity with a single metal ion only in the *cis* configuration (Fig. 2b). The *trans* configuration of this ligand (Fig. 2a) requires two complexing ions.

In view of the above-indicated possibility of using 2,2'-bi-1,10-phen in the reduced electron-excessive form as a component of novel tetraaza chromophore complexes, its electronic structure is of particular interest. A DFT calculation of the $(2,2'\text{-bi-}1,10\text{-phen})^{2-}$ anion demonstrated a decrease in the length of the C^9–C^{19} interfragment bond from 1.500 Å in the neutral ligand to 1.430 Å, and also an increase in the size of the cavity formed by the four nitrogen atoms (Fig. 3), suitable for insertion of a transition metal ion. Furthermore, the negative charges q_{N10} and q_{N20} on the nitrogen atoms that are the closest to the C^9–C^{19} interfragment bond increase, compared to those in the unreduced *cis* form, from –0.25 to –0.30 *e*, and the energy of the electron ionization from HOMO decreases from 6.00 to 3.35 eV. These factors should lead to a noticeable increase in the donor power of the reduced anionic form of 2,2'-bi-1,10-phenanthroline compared to the neutral ligand and favor insertion of complexing ions in its cavity.

Thus, our study showed that, in the anionic reduced electron-excessive form of the tetradentate ligand, $2,2'\text{-bi-}1,10\text{-phen}^{2-}$, both the geometric and electronic conditions are more favorable, compared to the neutral compound, for insertion of complexing ions in its cavity.

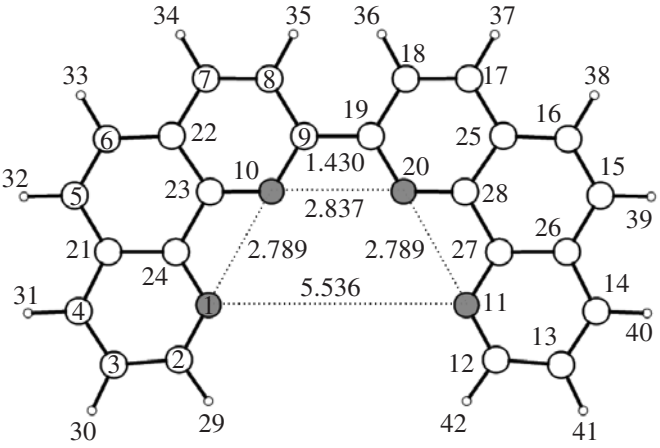


Fig. 3. Geometry of the cavity of the electron-excessive reduced form of the tetradentate ligand $(2,2'\text{-bi-}1,10\text{-phen})^{2-}$.

ACKNOWLEDGMENTS

The study was supported by the Russian Foundation for Basic Research (project no. 04-03-32932) and Departmental Target Program "Development of the Scientific Potential of Higher School" (project no. RNP.2.1.1.1277).

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