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Quantum Chemical Investigations of the π-Acceptor Ability of α-Diimine Ligands

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The bonding properties of α-diimine complexes of transition metals in low oxidation states are essentially determined by π-back donation. The energies of the lowest unoccupied molecular orbitals of the ligands have been used to estimate their acceptor ability. MO calculations of selected α-diimines are reported in the present paper. N-unsubstituted and apliphatic diimines are found to be better π-acceptors than 2,2′-bipyridine which is in agreement with experimental results. It turns out that the LUMO energies calculated by the NDDO method are a good measure for the π-acceptor behaviour of ligands with similar structure towards transition metal ions.

Introduction

The coordination chemistry of α-diimines has been established by F. Blau [1] who in 1888 prepared the heteroaromatic bases 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) and their metal complexes $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$. In the following time many other transition metal complexes of these ligands have been investigated extensively [2–5]. Of particular interest is the ability of these diimine ligands to stabilize metals in low oxidation states (see Herzog and Taube [2]). It has been concluded that the reasons for this behaviour are energetically low lying π^*-ligand orbitals which enable a back donation of electrons from filled d-metal orbitals to empty ligand orbitals.

New representatives of the α-diimine type were found by the discovery of the aliphatic diimines of glyoxal and biacetyl. In 1953 Krumholz prepared the iron(II) compounds of glyoxalbismethylimine and biacetylbismethylimine [6]. It turned out that their spectral and chemical properties are closely related to those of the complexes containing the aromatic ligands bipy and phen. Due to these spectral similarities it has been concluded that the aliphatic diimines are also good acceptors.

By preparing the iron(II) chelates of 2-pyridinealdehydemethylimine Busch and Bailar suceeded in finding the connection between the aromatic and aliphatic diimines [7].

Investigations of the solvatochromism of the absorption in the electronic spectra and of the spin densities at the coordination centers on diimine substituted $[Mo(CO)_4(N\text{–}N)]$ complexes (with N–N = α-diimine) by ESR spectroscopy have shown that aliphatic ligands are much more effective π-acceptors than the classical acceptor molecule 2,2′-bipyridine [8–10].

In the framework of our thermo- and photochemical investigations of oxalato/diimine mixed ligand complexes [11–13] we are interested in detailed information about the acceptor ability of different α-diimine-type ligands. In the present paper the LUMO energies of selected diimines calculated by suitable quantum chemical methods are reported.

Calculational Methods

The NDDO (neglect of diatomic differential overlap) method proposed by Pople and coworkers [14] was employed for the calculations. All the ligands have been considered in the *cis* configuration in which they coordinate. In this arrangement the interactions between the ligand nitrogen lone pairs should be important. The CNDO method [14] is not able to treat these directional effects correctly, because of the spherical symmetric orbital approximation and the complete neglect of differential overlap for the calculation of interaction integrals. Therefore, we preferred the NDDO formalism in which the one-center differential overlap is retained. Thus anisotropic components of the lone-pair interactions are taken into accout [15, 16]. Details of the NDDO method and the parametrization used in this work are described in ref. [17].

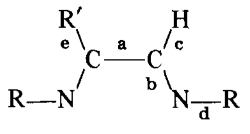
For the relatively large glyoxaldianil derivatives we chose the PPP method [18]. The following parameters have been applied:

$$C_{arom.}: I_C = -U_C = 11.42\text{ eV}; E_C = 0.58\text{ eV};$$
$$\gamma_{CC} = 10.84\text{ eV}; \beta = -2.318.$$

$$-N^{/\!/}: \quad I_N = -U_N = 14.12\text{ eV}; E_N = 1.78\text{ eV};$$
$$\gamma_{NN} = 12.34\text{ eV}.$$

The parameters for the substituents were taken from Gey [19]. Furthermore, for the two-center Coulomb repulsion integrals we adopted the Nishimoto–Mataga approximation [20] and the formula of Kon [21] for the β_{ij} of the N–C–C–N moiety.

The bond lengths for the aliphatic diimines employed were those from various structural determinations [22–24]. The bond angles are assumed to be 120°. For *o*-benzoquinonediimine and phenanthrenequinonediimine we used a standard geometry; for the remaining ligands see ref. [25].

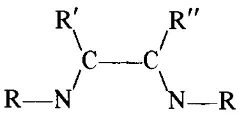


a = 0.146 nm d = $(N-CH_3)$ = 0.147 nm $(C-C)_{arom}$ = 0.140 nm
b = 0.129 nm $(N-C_{arom})$ = 0.146 nm $(C_{arom}-H)$ = 0.108 nm
c = 0.109 nm e = $(C-CH_3)$ = 0.152 nm $(C_{meth}-H)$ = 0.109 nm

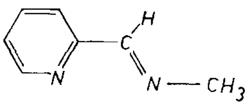
Results and Discussion

π-Acceptor Ability of Aromatic and Aliphatic Diimines

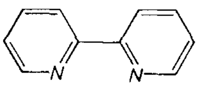
NDDO calculations of the following systems have been performed:



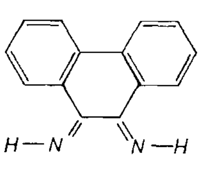
R' = R'' = H, R = H: α-diimine (dim)
R' = R'' = H, R = CH_3: glyoxalbismethylimine (gmi)
R' = R'' = H, R = Ph: glyoxaldianil (gda)
R' = H, R'' = CH_3, R = CH_3: methylglyoxalbismethylimine (mgmi)
R' = R'' = CH_3, R = CH_3: biacetylbismethylimine (bmi)



2-pyridinealdehydemethylimine (pmi)



2,2'-bipyridine (bipy)



9,10-phenanthrenequinonediimine (phi)

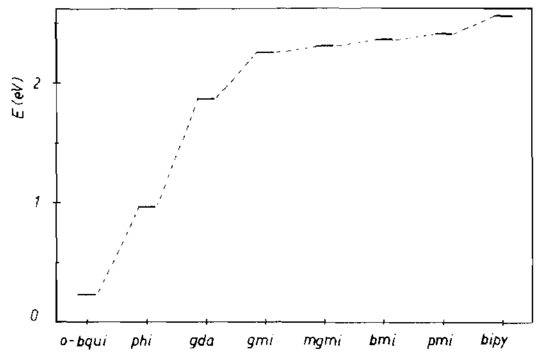
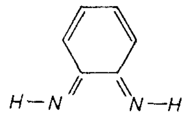


Figure 1. NDDO–LUMO energies of different α-diimine ligands.



o-benzoquinonediimine (*o*-bqui)

The ligands show no significant differences in view of σ-donation [25]. However, their metal complexes differ markedly in the spectroscopic (CT energies and solvatochromism) and electrochemical properties. Therefore, π-back donation has to play an important role.

The NDDO–LUMO energies are given in Fig. 1. This series of decreasing π-acceptor ability results:

$$o\text{-bqui} > \text{phi} > \text{gda} > \text{gmi} > \text{mgmi} > \text{bmi} >$$
$$> \text{pmi} > \text{bipy}.$$

It follows that bipy is a relatively poor π-acceptor ligand. The conclusion that aliphatic diimines are better acceptors than bipy corresponds to the experimental data of tom Dieck and coworkers on diimine mixed ligand complexes $[Mo(CO)_4(N\text{–}N)]$ [10]. 1,4-substitution as well as 2,3-substitution of dim by methyl group cause the LUMO energy to increase, whereas a marked stabilization results in the case of phenyl substitution. Assuming a planar geometry for the gda system, its LUMO energy is 0.82 eV lower than for gmi. However, it should be noted that the steric repulsion of the *o*-H atoms causes a distortion of the N-phenyl rings at 60° (lower total energy) [26] with a certain increase in the LUMO energy in comparison to the planar arrangement. The gradual destabilization of the lowest empty MO in the order gmi → mgmi → bmi is also valid for the various N-phenyl derivatives. A further enlargening of the aromatic system by 2,3-phenyl substitution (benzildiimines, *e.g.* in the case of gda → benzildianil) should not improve the acceptor behaviour because of the strong steric hindrance between the phenyl groups. This suggestion is supported by the hypsochromic shift of the lowest CT absorption in the benzildianil

TABLE I. NDDO–LUMO Energies, Longest CT Absorption of Diimine $Mo(CO)_4$ Complexes and Energies of the "Diimine Band" of the Corresponding $[Fe(N–N)_3]^{2+}$ Compounds.

	$\tilde{\nu}[Mo(CO)_4(N–N)]$ (cm^{-1}) in DMF [9]	$\tilde{\nu}[Fe(N–N)_3]^{2+}$ (cm^{-1}) [28]	LUMO Energy (eV)
o-bqui	–	14260 [29]	0.22
phi	–	13930	0.96
gda	17606	16340[a]	1.86[b]
gmi	20000	17970	2.24
mgmi	20986	–	2.30
bmi	21740	17720	2.34
pmi	–	18150	2.39
bipy	22500	19160	2.54

[a] Value of the biacetyldianil Fe(II) complex [30]. [b] N-phenyl rings 50° distorted.

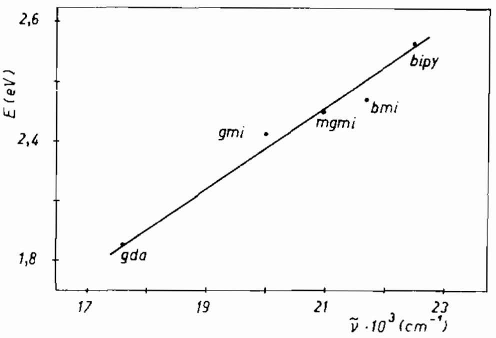


Figure 2. Correlation between NDDO–LUMO energies of diimine ligands and longest CT absorption of the corresponding $[Mo(CO)_4(N–N)]$ complexes (N–N = α-diimine).

$Mo(CO)_4$ complex in comparison to the analogous gda compound [27].

In bipy the aromatic stabilization results in a corresponding increase of the energy of the lowest antibonding orbital. The pyridine substituted ligand pmi is placed between aromatic and aliphatic ligands.

However, remarkably low lying LUMO energies have been found for the N-unsubstituted diimines *o*-bqui and phi. The preferential position of these ligands in respect to their acceptor ability is emphasized by the strong red-shifted CT absorptions (d–π* bands) of their iron(II) complexes [28, 29].

In Fig. 2 the correlation between the calculated NDDO–LUMO energies and the frequencies of the lowest CT absorption of the corresponding $[Mo(CO)_4(N–N)]$ compounds is shown. In Table I the energy of the "diimine band" of the $[Fe(N–N)_3]^{2+}$ complexes has been stated additionally.

Summarizing the presented results it can be concluded that the NDDO–LUMO energies are a suitable measure to estimate the π-acceptor capacity of molecules with similar structures.

The Influence of N-phenyl Substitution on the LUMO Energies of Glyoxaldianil

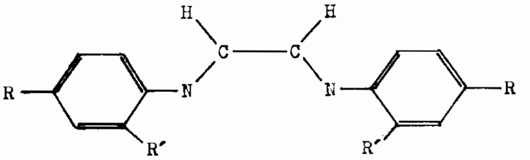
It turned out that gda is a relatively good acceptor ligand among the α-diimines. We investigated the influence of *o*- and *p*-substituents on the LUMO energy and on the charge distribution in the α-diimine skeleton of gda.

Unfortunately, these molecules are too large for the available NDDO program. Otherwise, they are

TABLE II. PPP–LUMO Energies, Net Charges in the N=C–C=N Moiety, Half-wave Potentials of the Free Ligand Reduction and Frequencies of the Longest CT Absorption of $[Mo(CO)_4(N–N)]$ Complexes (N–N = Substituted Glyoxaldianil).

	LUMO Energy (eV)	Net Charge		$E_{1/2}$ (V) [9]	$\tilde{\nu}$ $[Mo(CO)_4(N–N)]$ (cm^{-1}) in DMF [9]
		N	C		
I	–2.55	–0.144	0.137	–	17606
II	–2.47	–0.144	0.135	0.904	17621
III	–2.29	–0.142	0.130	0.932	17857
IV	–2.20	–0.142	0.128	0.969	17699
V	–2.02	–0.141	0.123	1.085	18350
VI	–2.41	–0.143	0.133	–	–
VII	–2.48	–0.144	0.135	–	–
VIII	–2.51	–0.145	0.136	0.885	–
IX	–1.21	–0.154	0.088	–	–

conjugated systems, so we decided to apply the PPP method. The following ligands have been calculated:



R = H (I), CH_3 (II), OH (III), OCH_3 (IV), $N(CH_3)_2$ (V), F (VI), Cl (VII), NO_2 (IX)
R' = H, CH_3 (VIII)

In Table II the LUMO energies, the net charges in the diimine skeleton, the available reduction potentials of the free ligands and the frequencies of the lowest CT absorptions of their $[Mo(CO)_4(N–N)]$ compounds are given. In all cases a destabilization of the first antibonding MO arises despite inductive and mesomeric substituent effects. In Fig. 3 and 4 the correlations between the PPP–LUMO energies and the half-wave reduction potentials of the free ligands as well as the frequencies of the lowest CT absorption of the corresponding molybdenum complexes are shown.

It follows that neither *para-* nor *ortho*-substituents improve the π-acceptor capacity in agreement with the experimental data.

The cis–trans *Behaviour of Diimine Ligands*

The coordinated diimines necessarily exhibit a *cis* or a weakly distorted *cis* configuration, whereas the free ligands have a *trans* configuration. By quantum chemical studies it has been found that the potential curves of the *trans–cis* rotation for dim and gmi correspond to the potential curve of similar conjugated systems, *e.g.* glyoxal [31] (the results for dim are: *cis–trans* difference 12.5 kJ/mol with the *trans* form as the more stable; rotation barrier 22.0 kJ/mol at 90° [32]).

In Fig. 5 we show the rotation behaviour of the NDDO–LUMO energies of the 1,4-diazabutadiene-like systems dim and bipy. It can be seen that in both cases the LUMO energy of the *trans* form is the more stable one (PPP calculations on dim show the same result). This contrasts with the opinion of some authors that these ligands in the coordinating *cis* configuration have the lower LUMO energies [10].

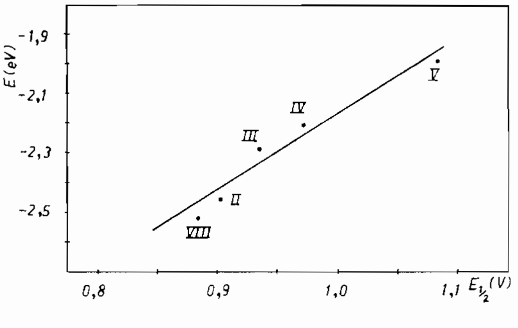


Figure 3. Correlation between PPP–LUMO energies of substituted glyoxaldianils and their reduction potentials.

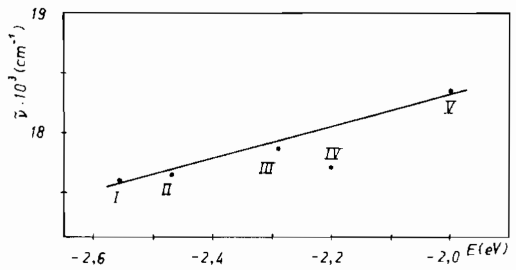


Figure 4. Correlation between PPP–LUMO energies of substituted glyoxaldianils and longest CT absorption of the corresponding $[Mo(CO)_4(N–N)]$ compounds (N–N = substituted glyoxaldianil).

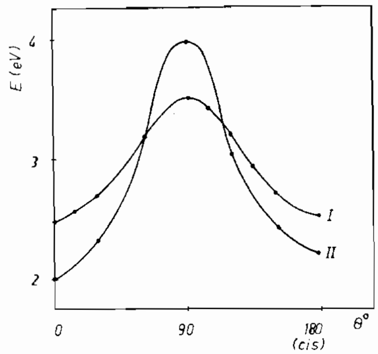


Figure 5. NDDO–LUMO energy as a function of the torsion angle θ. I = bipy; II = dim.

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