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Semi-empirical Molecular Orbital Studies of Dimethylglyoxime and the Dimethylglyoximate Anion

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The π-electron system of dimethylglyoxime(H_2D) and HD^- has been studied in the zero differential overlap approximation with semi-empirical choice of parameters. The evaluation of the one-electron matrix elements is based on studies on some small "model" molecules. The structure of the molecule in solution is discussed and the absorption spectra of the molecule and the anion are interpreted. The two absorption peaks of HD^- are assigned to $\pi-\pi^*$ transitions.

The crystal structure of dimethylglyoxime (H_2D) has been determined by X-ray diffraction by Merritt and Lantermann [1] and also with neutron diffraction by Hamilton.[2] The bond lengths and angles reported in the latter work have been used in this investigation (Fig. 1). H_2D crystallises in a *trans*-form as illustrated in the figure. It has been proposed [3] that H_2D solved in water also has this form. However, for H_2D solved in dioxane a dipole moment of 1.38 D has been reported.[4] This indicates that the configuration at least in dioxane is *cis*, where half of the molecule has been twisted 180° around the central C—C bond. Both configurations have been studied here and the results indicate clearly that the structure is *cis* also in water solutions. The *cis*-form is of special interest since it occurs in the metal chelates $Me(HD)_2$ which will be the object for later investigations.

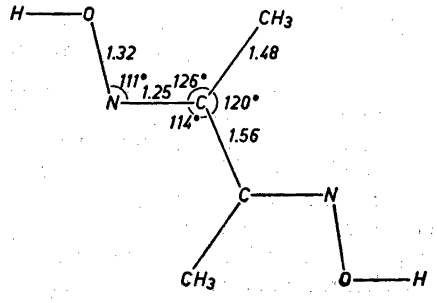

Fig. 1. Structure of dimethylglyoxime (H_2D), *trans*-form, after Hamilton.[2] Bond lengths in Å.

METHOD OF CALCULATIONS

The π-electron system, containing 8 π-electrons, of H_2D and HD^- has been studied within the LCAO-SCF approximation with assumed orthogonalized orbital basis and zero differential overlap, according to the method first outlined by Pariser and Parr.[5] Semi-empirical parameters have been used in order to calculate the matrix element of the Fock operator. It has been shown by Fischer-Hjalmars [6] that to the second order in the nearest neighbour overlap all parameters have local character. Accordingly, they should in this approximation be transferable from one molecule to another provided that the bonding scheme is similar. This method has been applied here and all core integrals have been estimated from calculations on some small model molecules. The semi-empirical parameters occurring are

$$W(\mu) = \langle \mu \mid T + U_\mu^+ + \sum_{\mu \neq \nu} U_\nu \mid \mu \rangle \tag{1}$$

$$\beta_{\mu\nu} = \langle \mu \mid H^{\text{core}} \mid \nu \rangle = \tfrac{1}{2} S_{\mu\nu} \{ A(\mu) + A(\nu) \} \tag{2}$$

$$\gamma_{\mu\nu} = (\mu\mu \mid \nu\nu). \tag{3}$$

Here μ denotes a π orbital on atom μ, U_μ^+ the potential from a unity charged atom μ. The third term in (1) contains penetration intergrals between orbital μ and neutral neighbours ν. When $W(\mu)$ is evaluated semi-empirically, it is important do this on a model molecule where atom μ has a similar surrounding in order to represent the penetration terms as correctly as possible. Also the core potential U_μ^+ is influenced by this choice. As has been pointed out by Sidman [7] the stabilization of the core-electrons through the sigma bonds will decrease the stability of the π-electrons compared to the atomic valence state. The use of atomic valence state ionization potentials for $W(\mu)$ is thus not consistent with the theory.

The diagonal elements of the core operator is given by

$$\alpha_\mu = \langle \mu \mid H^{\text{core}} \mid \mu \rangle = W(\mu) - (n_\mu - 1)\, \gamma_{\mu\mu} - \sum_{\nu \neq \mu} n_\nu\, \gamma_{\mu\nu} \tag{4}$$

where n_μ is the number of π-electrons on atom μ. The Goeppert-Mayer, Sklar [8] technique has been used to reduce the neighbour core potential to zero charge. This technique has also been used for the center μ itself in the case where the charge of the core is larger than unity. We prefer to use this method instead of using higher ionization potentials. The orbitals in positive ions are contracted, which should not be the case in the molecule, where the real charge is around zero.

Formula (2) for the resonance integrals $\beta_{\mu\nu}$ between nearest neighbours has been proposed by Fischer-Hjalmars [6] who also has shown that the parameters $A(\mu)$ have local character and thus are transferable. It should, however, be pointed out that $A(\mu)$ is not related to $W(\mu)$ in a simple way, but should be treated as an independent parameter. Thus (2) can be regarded as a generalization of the Wolfsberg-Helmholtz formula [9] where only one parameter, the proportionality constant, is chosen empirically. Furthermore since (2) has been derived from the general expression by an expansion in the overlap integral, it is related to the other approximations made in the ZDO-method in a theoretically more satisfying way.

TWO-ELECTRON INTEGRALS

The one-center two-electron integrals $\gamma_{\mu\mu}$ have been calculated under the assumption that the differences between the values obtained from Slater orbitals and the corresponding semi-empirical values are equal through a series of elements.[10] This "correlation" energy can be calculated if another assumption is introduced, namely that the theoretical values of the Slater-Condon parameters $F_0(pp)$ and $F_2(pp)$ calculated from Slater orbitals are proportional to the semi-empirical values, where the semi-empirical values for $F_2(pp)$ have been taken from the tables by Pilcher and Skinner.[11] If this is done for a series of elements from F^+ to O^- we get an approximately constant "correlation" energy. The mean value has been used to reduce the theoretical values of $\gamma_{\mu\mu}$. These values are found in Table 1.

Table 1. Semi-empirical values of $\gamma_{\mu\mu}$ in eV.

Element	C^+	C	C^-	N^+	N	N^-	O^+	O	O^-
$\gamma_{\mu\mu}$	13.84	11.97	10.11	17.30	15.43	13.57	20.76	18.89	17.03

As is seen from this table the one-center two-electron integrals are rather strongly charge dependent. This fact can not be ignored, when doing calculations on ions, where some atoms have charges appreciably different from zero. It is found that $\gamma_{\mu\mu}$ depends linearly on the charge Z_μ in the same way for all the elements. The following relation is valid

$$\gamma_{\mu\mu}(Z_\mu) = \gamma_{\mu\mu}(0) + 0.0685\, Z_\mu \tag{5}$$

The expression (5) has been used in the calculations on the ion HD^{--}. It was found that the incorporation of charge dependency in the two-electron integrals improved the results considerably.

Many different methods have been used to estimate the two-center two-electron integrals. The most common method is probably the interpolation procedure introduced by Pariser and Parr,[5] where $\gamma_{\mu\nu}(R)$ is given as a second degree polynomial in R, and the coefficients are determined by fitting the curve to $1/R$ for large values of R. Recently Fischer-Hjalmars [10] has suggested a less arbitrary method in which the "correlation energy" is calculated from a valence bond treatment of the H_2 molecule. Here another more simple method has been used. The two-center Coulomb intergrals $\gamma_{\mu\nu}(R)$ are written in the form

$$\gamma_{\mu\nu}(R) = \tfrac{1}{2}(\gamma_{\mu\mu} + \gamma_{\nu\nu})\, f(z) \tag{6}$$

where $z = \frac{1}{2}(\gamma_{\mu\mu} + \gamma_{\nu\nu})\, R$. If Slater orbitals are used it is easily seen that $f(z)$ is independent of the orbital exponents. This is exactly true only if they are the same. However, the variation is very small even if this is not the case. The same function $f(z)$ has therefore been used for all intergrals. One suggestion is to use the theoretical value of $f(z)$ based on Slater orbitals. This has not been done here but a simplified analytical expression for $f(z)$ has been assumed.

The function $f(z)$ should have a maximum equal to unity for $z = 0$, and equal $1/z$ for $z \gg 1$. The following function has these properties

$$f(z) = 1 / (z + e^{-z}) \tag{7}$$

This function has been used to determine the two-center integrals $\gamma_{\mu\nu}$. A function $f(z)$ which almost exactly reproduces the theoretical values found with Slater orbitals for equal orbital indices is

$$f(z) = 1.3 / [1.3z + (1.3-z)\ e^{-0.2308\ z}] \tag{8}$$

Calculations for ethylene with $R = 1.337$ Å give, using (7), (8) and the method given by Fischer-Hjalmars, $\gamma_{12} = 8.31$, 9.78, and 8.09 eV, respectively. If these values, together with the one-center integral for carbon given in Table 1, are used to calculate the singlet-triplet separation in ethylene, which only depends on the two-electron integrals, this yields 3.66, 2.19, and 3.88 eV, respectively, to be compared with the experimental value 3.02 eV.

CHOICE OF SEMI-EMPIRICAL ONE-ELECTRON PARAMETERS

The parameters $W(\mu)$ and $A(\mu)$ have been evaluated from calculations on "model" molecules. In these calculations the one-center two-electron integrals are given values tabulated in Table 1, and eqn. (7) is used for the two-center integrals. It is important to emphasize this since the numerical values of the one-electron integrals depend on the method used in the calculations of the two-electron integrals.

The values for carbon were estimated from calculations on ethylene and benzene. In ethylene the first singlet-singlet transition and the first ionization potential, which have been found to be 7.62 [12] and 10.52 eV,[13] respectively, were used to calculate $A(\pi_C)$ and $W(\pi_C)$. This yielded $W(\pi_C) = -9.34$ eV (to be compared with the atomic valence state IP, 11.52 eV) and $\beta_{CC} = -2.93$ eV, which gives $A(\pi_C) = -10.58$ eV. However, since the bonding of the carbon atom in ethylene is different from the bonding in H_2D, $A(\pi_C)$ was also calculated from the spectrum of benzene where it was chosen in order to fit the transition $^1A_{1g} \rightarrow {}^1B_{2u}$ at 4.86 eV.[24] This gave $\beta_{CC} = -2.33$ eV. $W(\pi_C)$ was kept at the value -9.34 eV. Since the calculated ionization potential of benzene agreed with experiment (experimental value 9.25 eV,[14] calculated value 9.22 eV), this value is probably correct also for benzene. From β_{CC} the value -9.49 eV was obtained for $A(\pi_C)$. This value seemed to be more appropriate and was used in the calculations on H_2D and HD^-.

The parameters for oxygen were estimated from calculations on formaldehyde, where the parameters obtained from ethylene were used for carbon. The empirical information used was the first π-electron IP 11.8 eV [15] and the $\pi-\pi^*$ transition at 7.95 eV.[16] $W(\pi_O)$ was found to be -14.36 eV (valence state IP = 17.25 eV), which is exactly the same fraction of the atomic valence state IP as found for carbon in ethylene. However, this value was not used for $W(\pi_O)$ in H_2D since the core state is not the same. Instead $W(\pi_O)$ has been taken from the first IP of C_2H_5OH, which is 10.63 eV.[14]

For the negatively charged oxygen in HD^-, however, $W(\pi_O)$ from CH_2O has been used. The two parameters are related through two-electron integrals in the following way:

$$W(\pi_O)_{CH_2O} = W(\pi_O)_{C_2H_5OH} + J_{\sigma\pi} - J_{\pi\pi} - \tfrac{1}{2} K_{\sigma\pi} \quad (9)$$

If the two-electron integrals are evaluated by similar methods as described above, this equation gives $W(\pi_O)_{CH_2O} = -13.4$ eV which is in good agreement with the calculated value.

For β_{CO} the value -2.95 eV was obtained. This gives $A(\pi_O) = -17.41$ eV.

The parameter $A(\pi_N)$ was estimated, from the $\pi-\pi^*$ transition at 4.94 eV [17] in pyridine, to be -12.37 eV, with $\beta_{CN} = -2.34$ eV. In these calculations the value -10.20 eV was used for $W(\pi_N)$, which was obtained from the atomic valence state IP by scaling with the factor that was determined from the calculations on C_2H_4 and CH_2O. $W(\pi_N)$ in pyridine is related to the molecular IP of for example $(C_2H_5)_3N$ through a relation similar to (9). With such a relation one obtains, with IP of $(C_2H_5)_3N$ equal to 7.84 eV,[14] $W(\pi_N) = -10.11$ eV which is in agreement with the used value.

The semi-empirical parameters used in the calculations on H_2D and HD^- are collected in Table 2.

Table 2. Semi-empirical one-electron parameters for H_2D and HD^- in eV.

$W(\pi_O') = -14.36$ [a]	$A(\pi_O) = -17.41$	$\beta_{NO} = -2.07$
$W(\pi_O) = -10.63$	$A(\pi_N) = -12.37$	$\beta_{CN} = -2.75$
$W(\pi_N) = -10.20$	$A(\pi_C) = -9.49$	
$W(\pi_C) = -9.34$		$\beta_{CC} = -1.75$

[a] Value for the deprotonized oxygen in HD^-.

GROUND STATE PROPERTIES

The computations were performed on UNIVAC 1107 by means of a SCF-CI program made by Mr. Peter Eisenberger, and completed by Mr. Torbjörn Alm, which was kindly put at my disposal.

The MO-energies for H_2D-*cis* and HD^--*cis* are represented in Fig. 2. The scheme is very similar for the *trans* configuration. The details of these results will not be given here, only the points of main interest will be discussed.

The highest occupied orbital in H_2D has the energy -7.74 eV for the *trans* and -7.84 for the *cis* configuration. These values thus correspond to the first ionization potential of H_2D. Unfortunately there is at the time no experimental information available on this point. This would have been of great interest in order to test the parameter choice, since the ionization potential is very sensitive to this.

The bond orders are almost the same for the *cis*- and the *trans*-form, and have the values indicated in Fig. 3, where also the net charges due to the π-electron distribution are given in atomic units.

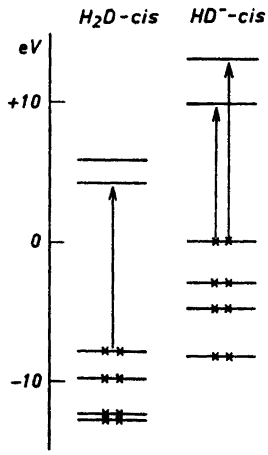

Fig. 2. MO-energies of H_2D-*cis* and HD^--*cis*.

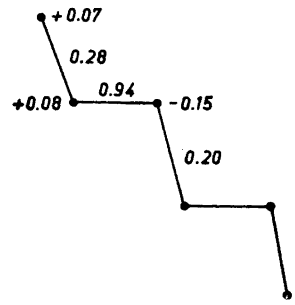

Fig. 3. Charges and bond orders for H_2D-*trans*.

The calculated high bond order of the bond C—N is in agreement with the short distance of this bond. The C—C bond order should indicate a normal single bond distance as for example in butadiene (1.48 Å). With Coulson's [18,19] linear relationship between C—C bond distances and bond orders one obtains the C—C distance 1.48 Å. It should be noticed that the long C—C distance 1.56 Å given by Hamilton [2] was used to calculate all matrix elements. As a matter of fact the choice of bond distances for the calculation does not seem to affect the obtained bond orders appreciably.[19] The long C—C distance of 1.56 Å reported by Hamilton is surprisingly large. Merritt and Lantermann have in their X-ray diffraction measurements found the distance to be 1.44 Å.[1]

The total energy for the π-electron system was calculated to -114.3 eV for the *trans* form and -114.0 eV for the *cis* form. These energies incorporate the core repulsion energy, which was estimated in a point charge approximation. The two-configurations are thus found to have almost the same stability, differences in steric repulsion not being considered.

For the dipole moment of the *cis* form the value $\mu_\pi = 1.51$ D was obtained. This is in good agreement with the experimental value 1.38 D, if it is assumed that the σ-electrons do not give any considerable contribution to the total dipole moment. A quantitative estimate of μ_σ is difficult to make and must contain many uncertain assumptions. It could however, be stated with some confidence that the main contribution to μ_σ comes from the lone-pairs and that the contributions from the bonds are small. Since the lone-pair on oxygen in H_2D has almost opposite direction to the nitrogen lone-pair, the moments from them should cancel, leaving a σ moment of some tenths of a Debye.

SPECTRA

The spectrum of H_2D dissolved in perchloric acid has been measured by Burger *et al.*[20] who reported a strong absorption band with a maximum at 44600 cm^{-1} and an extinction coefficient of 1.1×10^4. From their published absorption band, the oscillator strength has been estimated to ~ 0.3. Dyrssen and Petković[21] have measured the absorption spectrum of H_2D dissolved in water. They report a strong absorption band with a maximum at 44520 cm^{-1} and an extinction coefficient of 1.4×10^4. The oscillator strength is here 0.43. A program for resolution of absorption spectra, constructed by the author,[22] has been used to calculate the individual band characteristics. Burger *et al.* also measured the spectrum of H_2D in 0.2 M NaOH solution. They have found two absorption bands with maxima at 37700 cm^{-1} and 45800 cm^{-1}, and extinction coefficients of 1.79×10^4 and 1.59×10^4, respectively. The oscillator strengths have been estimated, by the present author, to ~ 0.4 and ~ 0.1, respectively. According to Burger *et al.*, this is the spectrum of the singly charged ion HD^-. However, it has been pointed out by Dyrssen[3,23] that in solutions with pH above 12 the doubly charged ion D^{2-} dominates. This is clearly the case here and the absorption spectrum quoted thus corresponds to this ion.

The absorption curves of the metal chelates $Me(HD)_2$ contain two strong bands which, with great certainty are due to $\pi-\pi^*$ transitions in the chelate ring. Thus the spectrum of $Cu(HD)_2$ dissolved in water contains one band with maximum at 44550 cm^{-1} and with an oscillator strength of 0.47, and a second band with maximum at 37520 cm^{-1} with the oscillator strength 0.33.[21,22] Corresponding bands occur for other metal chelates.

Table 3. Spectra of H_2D, HD^- and D^{2-}.

	theor.		exp.[a]		exp.[b]	
	ν cm^{-1}	f	ν cm^{-1}	f	ν cm^{-1}	f
H_2D- *trans*	50 000	0.94	44 600	~0.3	44 520	0.43
H_2D- *cis*	46 820	0.37				
HD^-- *trans*	39 070	0.60	—	—	37 520[c]	0.33
HD^-- *cis*	38 560	0.44				
HD^-- *trans*	50 890	0.12	—	—	44 550[c]	0.47
HD^-- *cis*	50 460	0.16				
D^{2-}- *trans*	43 470	0.79	37 700	~0.4	—	—
D^{2-}- *cis*	42 690	0.51				
D^{2-}- *trans*	51 000	0	45 800	~0.1	—	—
D^{2-}- *cis*	51 290	0.23				

[a] Burger *et al.*
[b] Dyrssen and Petković.
[c] From the spectra of $Cu(HD)_2$ dissolved in water.

The $\pi-\pi^*$ transitions in H_2D and HD^- have been calculated with configurational interaction taking into account all singly excited configurations. The lowest singlet-singlet transition of H_2D and the two lowest transitions of HD^- are found in Table 3 together with the experimental information.

The transition at 50000 cm^{-1} in H_2D-*trans* is assigned as $^1A_g \rightarrow {}^1B_u$, and is polarized in the molecular plane. The corresponding transition in the *cis*-form is assigned as $^1A_1 \rightarrow {}^1B_1$, and is polarized along the two-fold symmetry axis of the molecule. This difference in polarization explains the great difference in oscillator strengths between the *cis*- and *trans*-form. It might be dangerous to use comparatively uncertain theoretical results in order to draw conclusions about the structure. However, the obtained results for the *cis*-configuration agree markedly better with experiments than the results for the *trans*-configuration. Especially this is the case for the oscillator strengths which strongly depends on the molecular symmetry.

The two lowest transitions found for HD^- are in agreement with the two strong absorption bands in the metal chelates (Table 3). The assignments of these bands to $\pi-\pi^*$ transitions in the chelate ring are thus in agreement with the present results.

In order to study the spectrum of H_2D in 0.2 M NaOH solution given by Burger *et al.*, calculations have also been made on D^{2-}. The calculated spectrum of this ion differs very little from the calculated spectrum of HD^- (Table 3). It could be noticed that, as a consequence of the symmetry of D^{2-}, the transition found at 51000 cm^{-1} is forbidden for the *trans*-form. This transition must, however, be associated with the absorption band at 45800 cm^{-1}, with an oscillator strength of ~ 0.1, found by Burger *et al.* This band could not arise from the single charged ion HD^- since, according to the acidity constants given by Dyrssen,[2] the concentration of this ion in 0.2 M NaOH solution should be too small. The oscillator strength of this band thus indicates that the configuration of D^{2-} is *cis*.

All the calculated transition frequencies are found to be somewhat too high. Partly this is probably due to solvent effects. The $A(\pi_O)$ value used for oxygen is, however, a little problematic. Since it was determined from the localized double bond of formaldehyde it might be too high, as was found to be the case for the corresponding carbon parameter estimated from the double bond in ethylene.

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REFERENCES

1. Merritt, L. L. and Lantermann, E. *Acta Cryst.* **5** (1952) 811.
2. Hamilton, W. C. *Acta Cryst.* **14** (1961) 95.
3. Dyrssen, D. *Svensk Kem. Tidskr.* **75** (1963) 618.
4. Milone, M. *Gazz. Chim. Ital.* **65** (1935) 94.
5. Pariser, R. and Parr, R. G. *J. Chem. Phys.* **21** (1953) 466.
6. Fischer-Hjalmars, I. *To be published in Advan. Quantum Chem.* **2** (1965).
7. Sidman, J. W. *J. Chem. Phys.* **27** (1957) 429.
8. Goeppert-Mayer, M. and Sklar, A. L. *J. Chem. Phys.* **6** (1938) 645.
9. Wolfsberg, M. and Helmholtz, L. *J. Chem. Phys.* **20** (1952) 837.
10. Fischer-Hjalmars, I. In Löwdin, P.-O. and Pullman, B. *Molecular Orbitals in Chemistry, Physics and Biology*, Academic Press, New York 1964.
11. Pilcher, G. and Skinner, H. A. *J. Inorg. Nucl. Chem.* **24** (1962) 937.
12. Evans, D. F. *J. Chem. Soc.* **1960** 1735.
13. Field, F. H. and Franklin, J. L. *Electron Impact Phenomena*, Academic Press, New York 1957.
14. Al-Joboury, M. I. and Turner, D. W. *J. Chem. Soc.* **1964** 4434.
15. Sugden, T. M. and Price, W. C. *Trans. Faraday Soc.* **44** (1948) 116.
16. Walsh, A. D. *Trans. Faraday Soc.* **42** (1946) 66.
17. Mason, S. F. *J. Chem. Soc.* **1959** 1247.
18. Coulson, C. A. *Victor Henri Memorial Volume*, Desoer, Liege 1948, p. 15.
19. Skancke, P. N. *Acta Chem. Scand.* **19** (1965) 401.
20. Burger, K., Ruff, I. and Ruff, F. *J. Inorg. Nucl. Chem.* **27** (1965) 179.
21. Dyrssen, D. and Petković, D. *Acta Chem. Scand.* **19** (1965) 653.
22. Roos, B. *Acta Chem. Scand.* **18** (1964) 2186. (The program is available at the Inst. of Theor. Phys., Vanadisväg. 9, Stockholm Va).
23. Dyrssen, D. *Private Communication.*
24. Clar, E. *Aromatische Kohlenwasserstoffe*, 2nd Ed., Springer-Verlag, Berlin 1952.

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