



Available online at: www.basra-science-journal.org

ISSN -1817 -2695



Application of electrostatic Solvent Models to the Electronic Spectrum of Mesityl Oxide

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Accepted 20-1-1997

Abstract

MNDO method has been carried out to determine the most stable structure of the two conformers of mesityl oxide. The final optimized geometry of the stable conformer was used as input data for CNDO/S-CI solvent models. Four models depending on the effective virtual charge were used to study the effects of non-specific interactions between the mesityl oxide (solute) and solvent on electronic spectrum of the studied molecule. These models are Germer Model (GM), Tapia Model (TM), Modified Solvaton Model (MSM) & Modified Tapia Model (MTM). CNDO/S results showed that GM was not successful whereas TM has correctly predicted the blue shift on $^1(n\pi^*)$ state but it failed for $\pi \rightarrow \pi^*$ transition. MSM & MTM gave good results for the effects of solvent on the electronic spectrum which indicate a blue shift for $n \rightarrow \pi^*$ and a red shift for $\pi \rightarrow \pi^*$ transitions when the polarity of the solvent increases, and these results are in excellent agreement with experimental data of solvent effects, but the results of MSM are more precise than that of MTM. These results are also interpreted by the dipole moments values of the ground state (1so) and $^1(n\pi^*)$ and $^1(\pi\pi^*)$ excited states.

Introduction

Electronic absorption spectra of α,β unsaturated ketones are characterized by an intense absorption band $\pi \rightarrow \pi^*$ in the 215-250 nm region (molar absorption coefficient, ϵ_{\max} is usually in the range of 10,000-20,000 and a weak band $n \rightarrow \pi^*$ at 310-330 nm (Cooper, 1980). The most common α, β unsaturated ketone is the mesityl oxide (Figure 1).

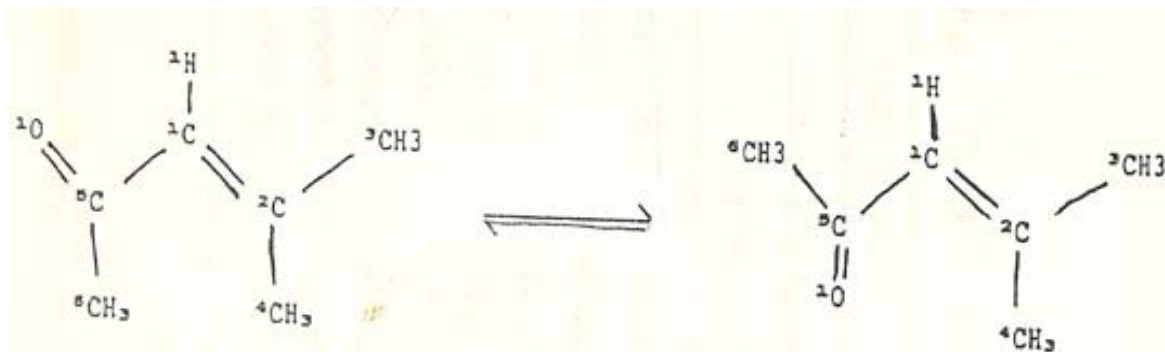
Brealey & Kasha (1955) concluded that the mesityl oxide have electronic transitions of $n \rightarrow \pi^*$ type that can be easily distinguished from $\pi \rightarrow \pi^*$ type by using solvent effect. It was found that if the non-polar solvent is replaced by a polar one, a measurable increase occurs in the energy of $n \rightarrow \pi^*$ transitions of the mesityl oxide (blue shift)

while $\pi \rightarrow \pi^*$ transitions are liable to a decrease in their energies (red shift). This effect is attributed to the specific and non-specific interactions between the mesityl oxide (solute) and solvent (Eichardt, 1979). The non-specific interactions can be studied by quantum mechanics (Tapia, 1980; Tapia, 1982), such studies comprise the effective charge (electrostatic) models.

The main objective of the present work was therefore to investigate the non-specific interactions between the mesityl oxide and the solvent and the inclusion of solvent effects in the theoretical calculations of the electronic spectrum of mesityl oxide. The equilibrium geometry of the mesityl oxide (Figure 1) was deduced by minimization of

the total molecular energy obtained by MNDO method (Dewar & Thiel, 1979). The optimal MNDO geometry of the stable conform (Figure 1) of mesityl oxide was used as input data for CNDO/S-CI

procedure in combination with the Germer Model (GM), Modified Solvaton Model (MSM) (Ebraheem et al., 1989) and Virtual Charge Model (Tapia Model, TM) (Tapia, 1982).



The MNDO procedure of Dewar and Thiel used in this investigation is a semi-empirical version of the NDDO approximation of the Roothan-Hall SCF-LCAO-MO method. The calculations were carried out with full geometry optimization. Starting geometries of the mesityl oxide conforms (Figure 1, A&B) were based on standard bond lengths and angles (pople & Gordon, 1967).

Theoretical representation of the non-specific interactions has been almost exclusively based on the dielectric continuum models (Pullman,1976) where the solute molecule is immersed in a continuously polarizable dielectric medium. In the present study, several approaches, such as GM, MSM and TM are used to incorporate the non-specific solvation effects within CNDO/S-CI method (Del Bene & Jaffe, 1968).

a. Germer Model (GM)

According to Germer Model, it is assumed that :

1. The solute molecule induce a number of charges (solvatons) in the solvent of dielectric constant (ϵ).
2. One solvaton is associated with each atom of the solute molecule, and its charge is

equal in magnitude but opposite in sign to the net charge of the atom to which it is attached.

3. There are no interactions between the solvatons.

The matrix elements of the Fock operator in the presence of the solvent (S) is given by :

$$F_{\mu\mu}^S = F_{\mu\mu}^o + D(\epsilon)V_A$$

(μ atomic orbital on atom A)

And

$$F_{\mu\nu}^S = F_{\mu\nu}^o + 0.5S_{\mu\nu}D(\epsilon)(V_A + V_B)$$

(μ on A & ν on B)

Where

$$V_A = \frac{Q_A}{r_A} + \sum_{B \neq A}^N \frac{-Q_B}{R_{AB}}$$

$$D(\varepsilon) = \frac{\varepsilon - 1}{2\varepsilon}$$

$F_{\mu\nu}^o$ are elements of the fock matrix in absence of the solvent, $S_{\mu\nu}$ is the overlap integral between μ and ν atomic orbitals, Q_A is the net charge on atom A, r_A represents the Paulings Van der Waals'

radius of the particular atom (Pauling, 1960), R_{AB} is the interatomic distance and $D(\varepsilon)$ is a function of dielectric constant (ε) of the solvent.

b. Modified Solvaton Model (MSM)

The MSM was described in detail elsewhere (Ebraheem et al., 1989). The

Fock matrix elements in presence of the solvent (S) are given by:

$$F_{\mu\mu}^S = F_{\mu\mu}^o + D(\varepsilon)V_A$$

(μ on A)

$$F_{\mu\nu}^S = F_{\mu\nu}^o$$

(μ on A & ν on B)

where

$$V_A = \sum_B^N \Gamma_{AB}^S$$

Γ_{AB}^S is the electron solvaton interaction integrals as previously described (Ebraheem 1989).

the calculation of the solvent dependence of nuclear spin-spin couplings $^1J(C-H)$ in acrylonitrile, acetaldehyde, acetone, chloromethanes and chloroethylenes (Ebraheem et al., 1989).

It has been recently demonstrated that INDO-SCPT procedure incorporating a MSM provides a satisfactory framework for

c. Tapia Model (TM)

TM was described in detail in Kadum et al.(1991). The elements of Fock matrix in presence of solvent (S) are given by:

$$F_{\mu\mu}^S = F_{\mu\mu}^o + D(\varepsilon)V_A$$

(μ on A)

$$F_{\mu\nu}^S = F_{\mu\nu}^o$$

(μ on A & ν on B)

where

$$V_A = \sum_B^N \gamma_{AB}$$

$$D(\varepsilon) = 1 - (\varepsilon)^{-0.5}$$

γ is the two centre electronic repulsion integral.

effects with the observed trends. (Kadum et al., 1991).

Recently, TM has been utilized in a study of solvent effects on the electronic structures and spectra of benzaldehyde and acetophenon. The results indicate a satisfactory interpretation of the medium

In this work, another expression is also used for the function $D(\varepsilon)$ with TM which is similar to that used in GM and MSM, i.e. $D(\varepsilon) = ((\varepsilon-1)/2\varepsilon)$ and for reason of comparison the model will be mentioned as MTM, in order to test these models and find

out which one provides best description for the non-specific solute solvent interactions. These models (GM, MSM, TM & MTM) are used to estimate the effects of solvent upon the electronic structure and spectrum

of the most stable conform of mesityl oxide (Figure 1 A) within CNDO/S-CI method. The calculations were carried out on IBM PS/2 model 60.

Results and discussions

MNDO calculations have been performed on both conforms of mesityl oxide (Figure

1). The final optimized geometries and heats of formation are listed in Table (1).

Table (1): MNDO optimized geometries and heat of formation of mesityl oxide conforms.

Geometric Parameters	Conform A	Conform B
Bond lengths		
C1→H1	1.097	1.102
C1→C2	1.360	1.358
C2→C3	1.516	1.518
C2→C4	1.508	1.507
C1→C5	1.494	1.500
C5→C6	1.530	1.526
C5→O1	1.228	1.232
Bond angles		
C1→C2→H1	117.34	115.86
C3→C2→C1	118.05	117.38
C4→C2→C1	125.10	126.53
C5→C2→C1	130.68	133.91
C6→C5→C1	116.17	123.44
O1→C5→C1	123.54	117.74
Heat of formation H ^f (Kcal/mole)	-38.4366	-34.4233
ΔE = ΔH ^{fB} - ΔH ^{fA} = 4.0133 (Kcal/mole)		

*Bond length in Å^o; angles in degrees, refer to Figure (1) for atoms numbering.

The value of ΔH^{fB} - ΔH^{fA} and found to be positives which suggests that the conform A should be more stable than B. The optimal MNDO geometry of mesityl oxide (conform A) was used as input data for CNDO/S-CI calculations to study the

effects of solvent on the electronic structure and spectrum of mesityl oxide.

CNDO/S calculations without solvation reveal a weak transition at 354. nm related to n→π*. A second transition of high intensity with wave length 222. nm is obtained and related to π→π*.

Solvent effects

Electronic spectrum

Table (2) exhibits the observed (Brealey & Kasha, 1955) and the theoretical CNDO/S results of the solvent effects on the electronic transition n→π* by using the GM, MSM and TM. Excluding the GM, these results indicate that n→π* transition suffer a blue shift if the solvent is replaced by more polar one. It can also be seen from Table(2) that TM gives a very high blue shift (Δλ = -55 nm), meanwhile the blue

shift predicted by MSM (Δλ = -25 nm) and by MTM (Δλ = -30 NM) are both comparable to corresponding observed one (Δλ = -22 nm). In contrast to the observed trend the GM predicts a red shift for n→π* transition. Table (2) shows that the oscillator strength f decreases as the polarity of the solvent increases by GM, MTM and MSM which are in agreement with the

experiment but the TM in this case makes an exception.

Table (2): CNDO/S and experimental results as a function of dielectric constant for ${}^1(n\pi^*)$ state of mesityl oxide.

Solvent	Dielectric constant	Solvent model								Experimental results(Brealey & Kasha, 1955)	
		MSM		GM		TM		MTM		λ	ϵ (m ² /mole) ^c
		λ^a	f^b	λ	f	λ	f	λ	f		
Hexane	2.02	335.	22.	361.	19.	327.	31.	331.	25.	327.	7.95
Chloroform	4.80	326	21.	372.	17.	290.	45.	315.	21.	-----	-----
Methanol	32.60	318.	20.	376.	16.	283.	52.	304	20.	312.	7.40
Water	78.30	309.	18.	379.	15.	272.	80.	301.	19.	305.	5.00
$\Delta\lambda = \lambda_{H_2O} - \lambda_{Hex.}$		-26.0		+18.0		-55.0		-30.0		-22.0	

- a) λ = wave length (nm)
 b) f = oscillator strength $\times 10^5$
 c) ϵ = molar absorption coefficient.

The observed results (Brealey & Kasha, 1955) and CNDO/S calculations of the effects of solvent upon the electronic transition $\pi \rightarrow \pi^*$ are summarized in Table (3).

The results obtained according to MSM ($\Delta\lambda = 14$ nm) and MTM ($\Delta\lambda = 8$ nm) indicate a red shift as the polarity of solvent increases from that of hexane to water, associated with a decrease of the oscillator strength f which are in good agreement with

observation of effects of solvent on $\pi \rightarrow \pi^*$ ($\Delta\lambda = 15$ nm). It should be noted that GM and TM could not succeed in prediction the right shift trend that both of which expect a blue shift for $\pi \rightarrow \pi^*$ transition when non polar solvent is replaced by a polar one.

Table (3): CNDO/S and experimental results as a function of dielectric constant for ${}^1(\pi\pi^*)$ state of mesityl oxide.

Solvent	Dielectric constant	Solvent model								Experimental results(Brealey & Kasha, 1955)	
		MSM		GM		TM		MTM		λ	ϵ (m ² /mole)
		λ	f	λ	f	λ	f	λ	f		
Hexane	2.02	227.	0.272	221.	0.249	224.	0.262	223.	0.264	229.5	126 0
Chloroform	4.80	233.	0.269	220.	0.244	222.	0.245	227.	0.260	-----	-----
Methanol	32.60	238.	0.266	219.	0.240	220.	0.237	229.	0.257	238.0	1070
Water	78.30	241.	0.263	218.	0.234	218.	0.211	231.	0.252	244.5	1000
$\Delta\lambda = \lambda_{H_2O} - \lambda_{Hex.}$		+14.0		-3.0		-6.0		+8.0		+15.0	

Dipole moments

The dipole moment of a solute molecule is known to be changed (ground and excited states) if the non polar solvent replaced by a polar one. This change arises from the net charge variation on the atomic centers of the solute. In case the dipole moment of the ground state of the solute molecule (μ_g) is

larger than that of the excited state (μ_e), increasing the polarity of the medium would results in a blue shift. This can be attributed to the fact that when the solvent replaced by more polar one the stability of the ground state would increase by an amount more $\mu_g - \mu_e$ occurring to the excited state. On the

contrary a red shift is expected in case the dipole moment of the excited state is greater than that of the ground state (Reichardt, 1980; Toeston & Schaad, 1974).

Table (4) shows the dipole moment variations of the ground state (1S_0), $^1(n\pi^*)$, and $^1(\pi\pi^*)$ excited states with increasing polarity of the medium by MSM, GM and MTM. GM has failed to predict both of the blue shift for $n \rightarrow \pi^*$ transition and the red

shift for $\pi \rightarrow \pi^*$ transition. For both MSM and MTM models, the calculations reveal that the dipole moment of the excited state ($^1(n\pi^*)$) is less than that of the ground state. Hence a blue shift is predicted by our calculations. It can also be seen from Table (4) that the dipole moment value for $^1(\pi\pi^*)$ excited state is greater than that of the ground state which gives an evidence for the red shift.

Table (4): CNDO/S results of dipole moments as a function of the dielectric constant for the ground, $^1(n\pi^*)$ and $^1(\pi\pi^*)$ excited states of mesityl oxide (in debye units).

Solvent	Dielectric Constant	Solvent Models					
		MSM		GM		MTM	
		μ_g^a	μ_{e1}^b	μ_g^a	μ_{e1}^b	μ_g^a	μ_{e1}^b
		μ_{e2}^c		μ_{e2}^c		μ_{e2}^c	
Hexane	2.02	4.184	3.277	4.056	3.644	4.542	3.221
Chloroform	4.80	5.960		4.307		5.783	
Methanol	32.60	4.404	2.870	4.185	3.702	5.107	2.930
Water	78.30	6.483		4.022		6.242	
		4.412	2.730	4.287	3.812	5.402	2.750
		7.103		3.834		6.504	
		4.535	2.552	4.364	3.970	5.923	2.642
		7.421		3.537		6.673	

- μ_g is the dipole moment of the ground state (1S_0)
- μ_{e1} is the dipole moment of the excited state $^1(n\pi^*)$
- μ_{e2} is the dipole moment of the excited state $^1(\pi\pi^*)$

Conclusions

Keeping in mind that investigation was on mesityl oxide, the following points are worth mentioning:

1. The GM has failed to predict the right shifts for this molecule.
2. Despite the fact that TM has correctly predicted the blue shift on $n \rightarrow \pi^*$ transition for this molecule in more polar solvent with overestimation. It failed to predict the red shift of $\pi \rightarrow \pi^*$ transition.

3. Both MTM and MSM predict the correct shifts in more polar media, a blue shift for $n \rightarrow \pi^*$ and a red shift for $\pi \rightarrow \pi^*$ transitions. The MSM appears to give the more precise results than MTM.
4. Finally more applications of these models on different other molecules need to be carried out for more examinations of these models.

References

- Brealey G.J. , Kasha M. (1955). "solvent effects on the electronic spectrum of mesityl oxide" J. Am. Chem. Soc. 77:4462.
- Cooper J. W. (1980). "Spectroscopic Techniques for Organic Chemists", John Wiley, New York.
- Del Bene J. , Jaffe H.H. (1968) "use of the CNDO method in spectroscopy" J. Chem. Phys. 48: 1805.
- Dewar M.J.S., Thiel W. (1979) "Modified Neglect of Diatomic Overlap Method" J. Am. Soc. 99:4893,4907.
- Ebraheem K.A.K., Shargi S. N., Kadum Sh. A. (1989). "INDO-SCPT calculation of solvent dependence on the spin spin coupling constant of chloro-methanes and chloroethylenes" , *Monat. Chemie* **120**: 923.
- Kadum S.A., Baker N.A., Al-Edanee T.E. (1991). "applications of the virtual charge model to the electronic structure and spectra of benzaldehyde and acetophenone", *Monat. Chemie* 122: 349.
- Kasha M. (1950) "Solvent effects on the electronic spectra of carbonyl compounds" *Faraday Soc. Disc.* 14(9) : 14.
- Pauling L. (1960) "The Nature of Chemical Bond", 3rd Ed. Cornell Univ. Press, Ithaca.
- Pople J.A., Gordon M. (1967) *J. Am. Chem. Soc.* 89:4253.
- Pullman A. (1979) In: Pullman B., Parr R. (eds.) "The New World of Quantum Chemistry (proceeding of the 2nd international Congress of Quantum Chemistry). Reidel, Dordrecht, pp. 149-187.
- Reichardt C. (1979) "Solvent Effects in Organic Chemistry", Verlag Chemie, Weinheim.
- Tapia O. (1980) In: Daudel R., Pullman A., Salem L. (eds.) "Quantum Theory of Chemical Reactions", Vol. 2. Reidel, Dordrecht, pp. 25-72.
- Tapia O. (1982) In: Ratajczak H., Orville-Thomas W.J. (eds.) "Molecular Interactions" Vol. 3. Wiley, New York, pp. 47-117.
- Toeston R., Schaad M. (1974) "Hydrogen Bonding", Marcel Dekker Inc., New York.