Monatshefte für Chemie 122, 1015–1018 (1991)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Energies of Excited States Calculated with MNDO and AM1

Peter Ertl

Chemistry Institute, Comenius University, CS-842 15 Bratislava, CSFR

Summary. Singlet excitation energies of 18 organic molecules have been calculated using MNDO and AM1 semiempirical methods with limited configuration interaction. While both procedures systematically overstabilize energies of excited states, the ordering of states and the effects of substituents are reproduced, with AM1 being slightly better suited than MNDO. The best agreement with experiment was obtained for conjugated systems.

Keywords. MNDO; AM1; Configuration interaction; Excitation energies; Excited states.

Energien für angeregte Zustände mittels MNDO- und AM1-Rechnungen

Zusammenfassung. Es wurden die Singlet-Anregungsenergien von 18 organischen Molekülen mittels der semiempirischen MNDO- und AM1-Methode mit beschränkter Konfigurationswechselwirkung berechnet. Beide Methoden zeigen eine systematische Überstabilisierung von angeregten Zuständen, die Reihenfolge der Zustände und die Substituenteneffekte werden jedoch gut wiedergegeben, wobei sich AM1 als etwas zuverlässiger erwies. Die beste Übereinstimmung wurde für konjugierte Systeme gefunden.

Introduction

Theoretical study of excited states is one of the most interesting but also most difficult tasks of quantum chemistry. Correlation effects play an even more important role than in the ground state and therefore ab initio calculations of excited states require inclusion of large basis sets and extensive configuration interaction. Therefore high quality ab initio calculations of excited states have so far been limited to small systems. Accordingly theoretical photochemistry is still a field for application of well parametrized semiempirical methods.

Currently there exist a large number of semiempirical parametrizations and almost all have been, with more or less success, used in theoretical photochemistry. A semiempirical procedure must properly describe both the ground state and excited state energy surfaces. However, specially parametrized spectroscopic methods, such as CNDO/S or LNDO/S, yield very good vertical absorption energies but fail in describing nonvertical areas of excited state hypersurface, as well as the properties of the ground state. Although CNDO/INDO methods correctly describe geometries of excited molecules, problems arise with conjugated or strained systems, and the worse in unrealistic overstabilization of $\sigma\pi^*$ and $\pi\sigma^*$ transitions. Parametrizations MNDOC [1] and SINDO1 [2] were used for the study of excited states with better success [3, 4].

The most used semiempirical methods currently are Dewar's group models MNDO [5] and AM1 [6]. In the study of ground state reactions they have displaced all other methods. Therefore they could also be proper candidates for the study of excited states. Such calculations, although quite rare, seem promising, indeed. Chiroptical properties of organic molecules [7], photochemical hydrogen shifts [8, 9], and various photoisomerizations [10–12] were calculated in this way. We have tested both methods for optimizing geometries of molecules in excited states, and especially AM1 has been shown to give very good results [13].

The goal of the present work was to calculate AM1 vertical excitation energies and compare them with experimental data and earlier MNDO results [14, 15]. We are aware of the fact that MNDO and AM1 cannot yield excitation energies of the same quality as specially parametrized methods, but unless these procedures have been shown to give at least the correct ordering of excited states, they cannot safely be used for study of reaction paths of photochemical reactions.

Calculations

MNDO [5] and AM1 [6] methods in standard parametrization were used for the calculations. We used the MOPAC-PC package [16] which we augmented by subroutines for configuration interaction (CI). Two types of CI were used, namely: (i) CI based on the SCF closed shell MOs, (SDCI) with inclusion of 6×6 monoexcited and limited number of biexcited configurations, and (ii) CI based on the half-electron MOs [17] (HECI) with inclusion of 6×6 monoexcited configurations from the reference open-shell singlet, (i.e. also some biexcited configurations from the closed shell ground state were used in this way). Although the extent of CI was very limited (total number of configurations used were 30–50), we believe that the results may provide useful indications to the reliability of the MNDO and AM1 methods for calculation of energies of excited states.

All excitation energies were calculated for optimized ground state geometries.

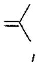
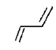
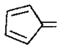
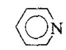
Results and Discussion

The calculated excitation energies for eighteen molecules of various structural types together with experimental data are listed in Table 1. Results are given for both MNDO and AM1, with two types of CI. An average absolute error in calculated spectra may be a criterion of reliability of particular treatments. That is for both, AM1 SDCI and AM1 HECI on the same level, about 0.9 eV. MNDO results are a little worse with an average absolute error exceeding 1 eV.

MNDO and AM1 were parametrized exclusively for proper description of ground state properties, and therefore we cannot expect results of the same quality as from specially parametrized spectroscopic methods. The overstabilization of excited states in MNDO was already reported by Dewar [18]. It is caused by overestimation of correlation energy through both parametrization and CI. Underestimation of the antibonding character of virtual MOs may also be important [19].

From Table 1 it can be seen that the best results were obtained for conjugated systems where errors are within 0.5 eV. On the other hand $\pi\pi^*$ transitions in isolated

Table 1. Vertical excitation energies (eV) calculated with MNDO and AM1

Molecule	State	MNDO SDCI	MNDO HECI	AM1 SDCI	AM1 HECI	Exp.	Ref.
$H_2C=CH_2$	B_{1u} $\pi\pi^*$	6.05	6.21	6.49	6.69	7.65	[23]
	A′ $\pi\pi^*$	5.78	5.98	6.07	6.30	7.19	[23]
	A_1 $\pi\pi^*$	5.59	5.80	5.86	6.06	6.74	[23]
	B_u $\pi\pi^*$	5.53	5.77	5.72	5.94	7.08	[23]
	B_2 $\pi\pi^*$	4.92	5.44	5.00	5.28	7.19	[23]
	B_2 $\pi\pi^*$	5.44	5.67	5.64	5.87	7.03	[23]
$H_2C=CHF$	A′ $\pi\pi^*$	5.64	5.76	5.87	6.02	7.19	[23]
$H_2C=CF_2$	A_1 $\pi\pi^*$	5.43	5.51	5.59	5.35	7.59	[23]
	A_g $\pi^2\pi^{*2}$	3.88	4.59	5.10	5.10	–	
	B_u $\pi\pi^*$	5.20	5.13	5.07	5.44	5.92	[24, 25]
	A_1 $\pi^2\pi^{*2}$	3.79	4.41	4.30	4.73	–	
	B_2 $\pi\pi^*$	4.31	4.23	4.51	4.47	5.20	[26]
	B_2 $\pi\pi^*$	3.14	2.69	3.31	2.89	3.44	[27, 28]
	A_1 $\pi\pi^*$	4.35	3.93	4.68	4.34	5.28	[27, 28]
$H_2C=O$	A_2 $n\pi^*$	3.13	2.81	2.94	2.61	4.20	[29]
$H_3CCH=O$	A″ $n\pi^*$	2.98	2.70	3.01	2.75	4.28	[30]
$Me_2C=O$	A_2 $n\pi^*$	3.08	2.57	3.31	2.86	4.48	[31]
$H_2C=CH-CH=O$	A″ $n\pi^*$	3.10	4.02	3.01	2.49	3.21	[32]
	A′ $\pi\pi^*$	5.40	5.54	5.68	6.01	6.40	[23]
$HC\equiv C-CH=O$	A″ $n\pi^*$	3.13	2.81	3.12	2.81	3.56	[33]
$O=CH-CH=O$	A_u $n\pi^*$	2.39	2.81	2.24	2.58	2.73	[32]
	B_g $n\pi^*$	3.21	3.08	3.26	3.15	3.71	[34]
	B_1 $n\pi^*$	5.05	5.17	4.39	4.57	4.31	[35]
	B_2 $\pi\pi^*$	4.19	4.35	4.40	4.75	4.70	[35]

double bonds are in some cases underestimated by more than 2 eV. However, the ordering of states is reproduced correctly.

Qualitative disagreement with experiment was obtained only in the case of pyridine: the ππ* state was predicted to be the lowest by MNDO, however, nπ* is the lowest one. Such incorrect ordering of states was also obtained with the MNDOC method [3]. AM1 yields the nπ* transition as the lowest.

On the basis of our results (Table 1) it can be said that although the methods under investigation overstabilize energies of excited states, they yield correct ordering of states and satisfactorily reproduce effects of substituents. AM1 gave slightly better results than MNDO. Both types of CI used are of about the same quality, but because relaxed excited state geometries are reproduced by half-electron orbitals much better [13], we recommend AM1 HECI. This method has been used successfully to study excited state processes, such as photoisomerizations around polar double bonds [20], and photoisomerization of pentadieniminium [21] and dimethylaminobenzonitrile [22].

References

[1] Thiel W. (1981) J. Am. Chem. Soc. **103**: 1413

[2] Nanda D. N., Jug K. (1980) Theor. Chim. Acta **57**: 95

[3] Schweig A., Thiel W. (1981) J. Am. Chem. Soc. **103**: 1425

[4] Mishra P. C., Jug K. (1982) Theor. Chim. Acta **61**: 559

[5] Dewar M. J. S., Thiel W. (1977) J. Am. Chem. Soc. **99**: 4899

[6] Dewar M. J. S., Zoebisch E. G., Healy E. F., Stewart J. J. P. (1985) J. Am. Chem. Soc. **107**: 3909

[7] Donkersloot M. C. A., Buck H. M. (1986) J. Mol. Struct. (Theochem.) **137**: 347

[8] Dormans G. J. M., Fransen H. R., Buck H. M. (1984) J. Am. Chem. Soc. **106**: 1213

[9] Dormans G. J. M., Peijnenburg W. J. G. M., Buck H. M. (1985) J. Mol. Struct. (Theochem.) **119**: 367

[10] Rullière C., Declémy A., Kottis Ph., Ducasse L. (1985) Chem. Phys. Lett. **117**: 583

[11] Troe J., Weitzel K. M. (1988) J. Chem. Phys. **88**: 7030

[12] Dormans G. J. M., Groennboom G. C., van Dorst W. C. A., Buck H. M. (1988) J. Am. Chem. Soc. **110**: 1406

[13] Ertl P. (1990) Collect. Czech. Chem. Commun. **55**: 1399

[14] Ertl P., Leška J. (1988) J. Mol. Struct. (Theochem.) **165**: 1

[15] Ertl P. (1989) Collect. Czech. Chem. Commun. **54**: 1433

[16] Olivella S.: MOPAC-PC, QCMP017

[17] Dewar M. J. S., Hashmall J. A., Venier C. G. (1968) J. Am. Chem. Soc. **90**: 1953

[18] Dewar M. J. S., Fox M. A., Campbell K. A., Chen Ch.-Ch., Friedheim X. X., Holloway M. K., Kim S. Ch., Liescheski P. B., Pakiari A. M., Thien T.-P., Zoebisch E. G. (1984) J. Comput. Chem. **5**: 480

[19] Baird N. C., Hadley G. G. (1986) Chem. Phys. Lett. **128**: 31

[20] Ertl P. (1990) Int. J. Quant. Chem. **38**: 231

[21] Ertl P. (1990) Collect. Czech. Chem. Commun. **55**: 2874

[22] Ertl P. (1990) Collect. Czech. Chem. Commun. **55**: 1891

[23] Robin M. B. (1974 and 1975) Higher Excited States of Polyatomic Molecules, Vols. I and II. Academic Press, New York

[24] Doering J. P. (1979) J. Chem. Phys. **70**: 3902

[25] Doering J. P., McDiarmid R. (1980) J. Chem. Phys. **73**: 3617

[26] McDiarmid R., Sabljič A., Doering J. P. (1985) J. Chem. Phys. **83**: 2147

[27] Domaille P. J., Kent J. E., O'Dwyer M. F. (1974) Chem. Phys. **6**: 66

[28] Straub P. A., Meuche D., Heilbronner E. (1966) Helv. Chim. Acta **49**: 517

[29] Chutjian A. (1974) J. Chem. Phys. **61**: 4279

[30] Hubbard L. M., Bocian D. F., Birge R. R. (1981) J. Am. Chem. Soc. **103**: 3313

[31] Rao C. N. R. (1967) Ultraviolet and Visible Spectroscopy. Plenum Press, New York

[32] Herzberg G. (1966) Electronic Spectra and Electronic Structure of Polyatomic Molecules. Van Nostrand, New York

[33] Howe J. A., Goldstein J. H. (1958) J. Am. Chem. Soc. **80**: 4846

[34] Kelder J., Cerfontain H., Eweg J. K., Rettschnick R. P. H. (1974) Chem. Phys. Lett. **26**: 491

[35] Innes K. K., Byrne J. P., Ross I. G. (1967) J. Mol. Spectrosc. **22**: 125

Received March 5, 1991. Accepted May 7, 1991