Semi-empirical molecular orbital and UV-Visible study of the charge transfer complex of 1-ethyl-4-(methoxycarbonyl) pyridinium iodide

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Abstract

Charge transfer complex of 1-ethyl-4-(methoxycarbonyl) pyridinium iodide is studied using AM1 semi-empirical calculations of molecular orbital model and UV-Visible techniques. The optimized geometry of 1-ethyl-4-(methoxycarbonyl) pyridinium cation showed a torsional angle, ϕ, 0.1° for the central C_1-C_2 bond between the cation and carbonyl group in the ground state, and the torsinal barrier (at ϕ = 80°, 100°) 2.0 kcal mol^{-1}. The optimized geometry of the complex showed a charge transfer between iodide and 1-ethyl-4-(methoxycarbonyl) pyridinium cation with different stability for ground and excited state. The values of the enthalpy of formation of the complex shows a strong interaction between the donor and acceptor comparing with the experimental data.

Introduction

When tetracyanoethene (white solid) and hexamethylbenzene (colorless) are mixed, an intensely perple solution is formed. This is due to the formation of a complex between the two components. its only one example of a large number of so-called electron-pair donor/electron-pair acceptor complexes (EPD/EPA complexes). Mulliken termed these absorptions "charge transfer (CT) absorptions" [1]. According to Mulliken's theory, the characteristic long-wavelength absorptions the formation of CT complex involves the delocalization of an electron from the HOMO of donor to the LUMO of the acceptor. The CT complex of 1-ethyl-4-(methoxycarbonyl) pyridinium iodide (EMCP)in solution was the first model process of empirical parameter of solvent polarity from spectroscopic measurement[2]. Generally, the characteristic coloration of different CT complexes as well as (EMCP) in solid phase seems due to the interaction between the N-hetroaromatic cation and different electron donor[3]. However, the geometry of minimum energy in solution or in gas phase due to the absence of the specific interactions related to packing effect present in a crystal. The quantum chemical calculations are applied to study CT complexes in order to obtain information on structure and other molecular properties of CT systems [4]. Semi-empirical calculations were used to demonstrate the ability to determine the stability of CT complexes. In these studies a good correlation was verified between the calculated standard heat of formation (ΔH^o_f) of CT complexes and experimental stability constant [4]. In present work, the interaction between iodide anion and 1-ethyl-4-(methoxycarbonyl) pyridinium cation is studied by molecular orbital calculations in *gas* phase using AM1 semi-empirical method. A molecular model for donor-acceptor pair is proposed, and the calculated molecular properties are correlated with the photo-physical behavior of the system in solution.

Computational and experimental methods

The molecular structure of iodide anion and 1-ethyl-4-(methoxycarbonyl) pyridinium cation were fully optimized using AM1 Hamiltonian as implemented in program (hyperchem 6) [5]. For the complex, the excited state energy was calculated by the half-electron method [6], without further geometry optimization. The determination of lowest energy structure of 1-ethyl-4-(methoxycarbonyl) pyridinium cation was obtained from angular parameters of rotational angle (α), torsional angle (ϕ) and inclination of methyl group (β), as showing in (Fig. 1)

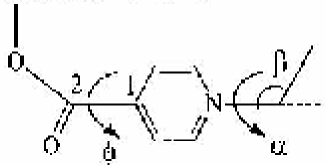


Fig. 1. Angular parameters used for geometry optimization of 1-ethyl-4-(methoxycarbonyl) pyridinium cation, where C_1-C_2 is central bond.

The geometry of lowest (ΔH^o_f) of the structure of 1-ethyl-4-(methoxycarbonyl) pyridinium cation was considered as the equilibrium conformation. The optimization of the (EMCP) complex was carried out from the optimized geometry of the components, and considering the intermolecular distance and torsional angle for over all structure of the complex. The starting geometry of the complex was built keeping the iodide near to pyridinium cation. The potential energy curves of complex in the ground and excited states with respect to the intermolecular distance between donor and acceptor were obtained by scanning of this parameters while the optimal geometry of each molecule remain constant for simplification. Thus, the energy difference between the ground and excited states would correspond to a vertical Frank-Condon transition [7].

Electronic absorption measurements were preformed on a Hitashi U-3501 spectrophotometer. 1-ethyl-4-(methoxycarbonyl) pyridinium iodide purchased from Aldrich Chemical Co.

Results and discussion

The acceptor structure of minimum energy was determined from torsional and rotational of the chemical groups of structure. This procedure was carried out due to the presence of several degree of freedom of 1-ethyl-4-(methoxycarbonyl) pyridinium cation, which could result in different local minimum energy configurations. The better combination among the angles (α, ϕ, β) producing a more stable geometry, is showing in (Fig. 2).

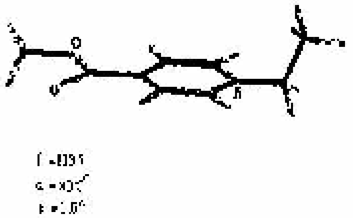


Fig. 2. Optimized geometry of 1-ethyl-4-(methoxycarbonyl) pyridinium cation using AM1 Hamiltonian as implemented in program (hyperchem 6) and it has C_1 symmetry.

The optimized geometry of 1-ethyl-4-(methoxycarbonyl) pyridinium cation has (β = 113.7°) and this value in agreement with the result reported from crystallographic data of 1-alkylpyridinium ring [8]. The rotation angle (α=88.7°) is relative to pyridinium group, and the dihedral angle (ϕ = 1.0°), resulting in a structure with C_1 symmetry (see in Fig. 2). The frontier orbitals of 1-ethyl-4-(methoxycarbonyl) pyridinium cation are π–type and exhibit degenerescence of the HOMO π-orbital. The LUMO is a non-degenerated orbital while iodide has a degenerescence of the HOMO non-bonding orbital. The energy values of frontier orbitals of the species are shown in Table 1.

Table 1. Frontier orbital energies (in eV) of 1-ethyl-4-(methoxycarbonyl) pyridinium cation and iodide were calculated from AM1 Hamiltonian.

Ion	Orbital	Energy
Pyridinium cation	HOMO	-14.7
	LUMO	-5.9
Iodide	HOMO	1.2
	LUMO	-

The (ΔH°_{f}) for the more stable geometry obtained for 1-ethyl-4-(methoxycarbonyl) pyridinium cation and iodide in ground state were 101.7 and -2.2 kcal mol^{-1}, respectively. The torsinal behavior of cation in gas phase was also studied by calculation of (ΔH°_{f}) as function of dihedral angle (ϕ). The tosional potential energy curve obtained form the data of (Table 2) is shown in Fig. 3.

Table 2. The calculated heat of formation (ΔH^{o}_{f}) for 1-ethyl-4-(methoxycarbonyl) pyridinium cation and dihedral angle (ϕ).

№	dihedral angle, ϕ, (degree)	ΔH^{o}_{f} (kcal/mol)	$\Delta\Delta H^{o}_{f}$ (kcal/mol)	№	dihedral angle, ϕ, (degree)	ΔH^{o}_{f} (kcal/mol)	$\Delta\Delta H^{o}_{f}$ (kcal/mol)
1	0	101.70	0.00	20	95	103.62	1.92
2	5	101.72	0.02	21	100	103.70	2.00
3	10	101.73	0.03	22	105	103.52	1.82
4	15	101.80	0.10	23	110	103.38	1.68
5	20	101.87	0.17	24	115	103.12	1.42
6	25	102.03	0.33	25	120	102.97	1.27
7	30	102.13	0.43	26	125	102.81	1.11
8	35	102.33	0.63	27	130	102.63	0.93
9	40	102.53	0.83	28	135	102.48	0.78
10	45	102.70	1.00	29	140	102.30	0.60
11	50	102.89	1.19	30	145	102.20	0.50
12	55	103.09	1.39	31	150	102.06	0.36
13	60	103.20	1.50	32	155	101.91	0.21
14	65	103.44	1.74	33	160	101.80	0.10
15	70	103.51	1.81	34	165	101.78	0.08
16	75	103.66	1.96	35	170	101.73	0.03
17	80	103.70	2.00	36	175	101.72	0.02
18	85	103.61	1.91	37	180	101.70	0.00
19	90	103.58	1.88				

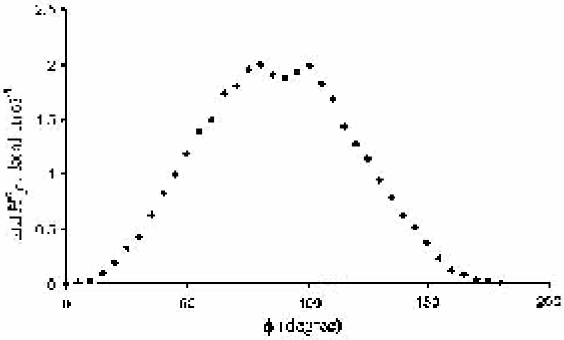


Fig.3. Torsional potential energy curve of 1-ethyl-4-(methoxycarbonyl) pyridinium cation in ground state obtained from calculation of (ΔH^{o}_{f}) using AM1 Hamiltonian.

The curve has a mirror image in the region of dihedral angle between 90° and 180° due to the C_1 symmetry of cation structure. Therefore, there is only one minimum energy conformation where (ϕ) has the value of 0.0°. The twist potential curve shows two barriers. The value of 2.0 kcal mole^{-1} obtained for the torsional energy barrier of the cation (at ϕ = 80°, 100°) is within the same value found for biphenyl from an ab initio STO-3G treatment [9] where the barrier reported in the range of 2.0-2.6 kcal mol^{-1}. The small barrier at 90° seems to be underestimated by the method used. However, the large electron affinity of the nitrogen atom reduces the electronic density on the C_1-C_7 central bond which generates a less effective π-bond torsional potential contribution decreasing the barrier high at ϕ =90°.

The results obtained show that the barrier are considerably low and therefore thermal rotation will take place in the gas phase as well as in a liquid phase in low viscosity.

Optimized geometry of (EMCP) complex is shown in (Fig. 4). The position of the iodide ion relative to pyridinium cation indicates its stronger interaction with pyridinium ring. The main factors responsible for this conformation are the CT interaction, these factors within charges and the distance between the cation and the anion of the CT complex and that make the pyridinium cation can accept one electron from iodide. Similar behavior was observed in CT complexes with pyridinium derivatives [10]. The structure of pyridinium cation changes slightly upon the (EMCP) complex. The rotation angles (α= 113.9°, β = 114.2°) and the torsional angle (ϕ = 4.8°).

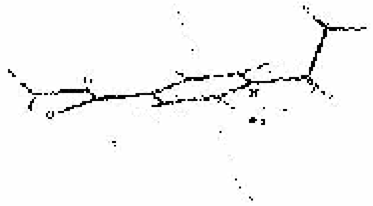


Fig. 4. Optimized geometry of (EMCP) complex, using AM1 Hamiltonian as implemented in program (hyperchem 6), the intermolecular distance (r_{DA}) at equilibrium (between N atom and I atom) is 3.9Å and the rotation angles (α= 113.9°, β = 114.2°) and the torsional angle (ϕ = 4.8°).

The intermolecular distance (r_{DA}) at equilibrium (between N atom and I atom) is 3.9Å. This value is within the range observed in organic CT complexes [1]. The (ΔH^{o}_{f}) obtained for the complex is 4.9 kcal mol^{-1}, which when subtracted from the sum of (ΔH^{o}_{f}) of the isolated components yields a stabilization energy of -94.6 kcal mol^{-1}. The experimental values of reaction enthalpy for formation strong CT complexes lie between -20 to -45 (kcal mol^{-1}) [11]. Both results indicate the formation of a strong complex and the difference may be described to the nature of the CT complex and the solvent effect.

Frontier orbital energies of (EMCP) complex of HOMO and LUMO orbitals are -2.23, -6.60 eV, respectively which were calculated from AM1 Hamiltonian. Fig. 5 shows the correlation diagram for the interaction between the HOMO of the donor and the LUMO of acceptor resulting in the stabilization and formation of the CT complex, in agreement with the Mulliken's theory, in addition to its components (data from Table 1).

This stabilization also can be recognized from presence of a CT absorption band of complex in methanol, as shown in Fig. 6. This electronic transition appears in a lower energy region compared with the absorption spectra of the components alone. The CT absorption band has a broad Gaussian shape. The CT complex from anion to cation in the reflecting the electron transfer from donor to acceptor in the excited state where HOMO orbital for iodide while LUMO orbital has a large contribution from pyridinium cation.

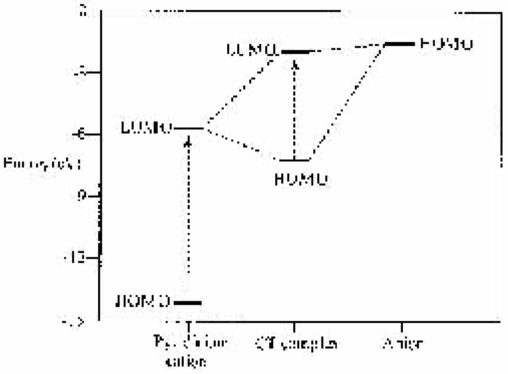


Fig. 5. Correlation for the formation of CT complex (EMCP) with its components

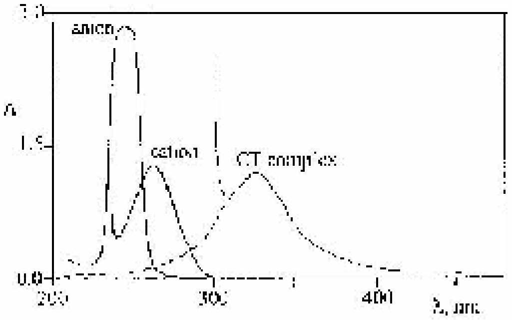


Fig. 6. Absorption spectra of pyridinium cation (5.10^{-5} M) λmax=286 nm, iodide (1.10^{-5} M) λmax=256 nm, and (EMCP) complex (0.01M) λmax=342 nm, in CH$_3$OH. Gaussian component of CT band (----).

The calculated potential energy curves of ground and excited states in gas phase as a function of molecular distance between pyridinium cation and iodide were obtained from the data of (Table 3) are given in (Fig. 7). In the ground state, the equilibrium intermolecular distance is 3.9 Å. In the excited state, the equilibrium intermolecular distance 6.0 Å is observed. and the stabilization energy is 2.2 kcal mol^{-1}, which is more less than that of ground state.

Table 3. Potential energies ($\Delta\Delta H^{\circ}_{f}$, kcal/mol) of ground and excited states in different intermolecular distance (r_{N-I}) (between N atom and I atom) for the (EMCP) complex.

Ground state		Excited state	
d(Å)	$\Delta\Delta H^{\circ}_{f}$ *	d(Å)	$\Delta\Delta H^{\circ}_{f}$
3.4	-51.8	3.4	53.90
3.5	-69.5	3.5	37.50
3.6	-81.6	3.6	25.80
3.8	-93.2	3.9	14.10
3.9	-94.6	4.1	8.60
4.0	-94.1	4.4	4.40
4.1	-92.4	4.6	3.30
4.2	-90.1	4.8	2.80
4.4	-84.1	5.0	2.30
4.6	-81.7	5.2	2.25
4.8	-76.1	5.5	2.20
5.0	-73.6	6.0	2.17
5.2	-70.7	6.5	2.18
5.5	-67.7	7.0	2.23
6.0	-64.2	7.5	2.28
6.5	-61.0	8.0	2.29
7.0	-58.7	9.0	2.30
7.5	-56.5	10.0	2.53

*The heat of formations (ΔH°_{f}) of the (EMCP) complex were subtracted from the sum of (ΔH°_{f}) of the isolated components for both cases of ground and excited states.

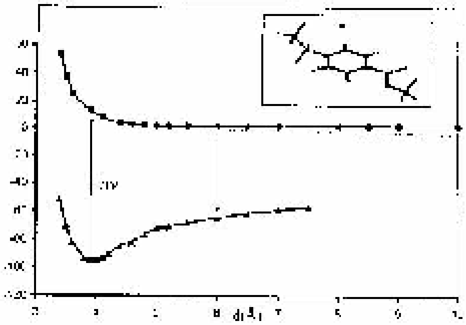
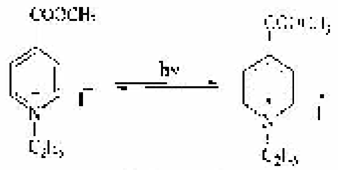


Fig.7. Potential energy curves of ground (▲) and excited (•) electronic states of (EMCP) complex, stabilization energy of the complex in the excited state at 6.0Å, Insert: Energy-optimized geometry of the CT complex from AM1 semi-empirical calculations.

The weak stability of the complex in the excited state can be described to an electrostatic repulsion effect of the neutral species due to electron transfer from the donor to acceptor forming two centers of radical, as represented by scheme 1.



Scheme 1

Conclusion

The interaction between iodide and 1-ethyl-4 (methoxycarbonyl) pyridinium cation forming a CT complex was investigated by computational and photo-physical techniques. The value of enthalpy of formation obtained for the complex in gas phase is within the range of formation of the strong CT complex. The heat of formation was used as a parameter to evaluate the stability of complex. UV Visible data and the optimization geometry showed a stable CT complex between iodide and the ring of pyridinium cation in ground state and less stability of CT complex was observed in excited state due to electron transfer from the donor to the acceptor which lead to formation of neutral species.

References

1. R.S. Mulliken, W.B. Person, Molecular Complexes, Wiley Interscience, New York, 1969.
2. E.M. Kosower, J. Am. Chem. Soc., 80, 3253, 1958; E.M. Kosower, J.A. Skorcz, W.M. Schwarz, J.W. Patton, J. Am. Chem. Soc., 82, 2188, 1960.
3. S. Sakanone. Y. Kai, N. Yasuka, N. Kasai, M. Kakudo, H. Mikawa, Chem. Commun., 1968, 176.
4. B.W. Clare, J. Mol. Struct., 337, 139, 1995.
5. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J.p. Stewart, J. Am. Chem.Soc., 107, 3902, 1985.
6. M. J. S. Dewar, N. Trinajstic, J.Chem. Soc., ,1220, 1970.
7. N. S. Isaacs, Physical Organic Chemistry, Longman Scientific & Technical, New York, Chap. 16, 1986.
8. S. Sakanone, Y. Kai, N. Yasuka, N. Kasai, M. Kakudo, Bull.Chem.Soc.Jap., 43, 1306, 1970.
9. G.H. Hafelinger, C. Regelmann, J. Comput. Chem., 6, 368, 1985.
10. Paul M.S. Monk, Neil M. Hodgkinson1, Robert D. Partridge, Dyes and Pigments, 43 (1999) 241.
11. C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, Wiely-VCH, Chap. 2, 2003.