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*m*PW1PW91 Calculated and Experimental UV/IR Spectra of Unsymmetrical *trans*-Stilbenes

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Quantum mechanical properties of unsymmetrical and unfunctionalized *trans*-stilbene derivatives **1-3**, which had been prepared by solid-phase parallel syntheses, were characterized using mPW1PW91/6-311G(d,p) (hybrid HF-DF) calculations. The total electronic energies, normal vibrational modes, Gibbs free energies, and HOMOs and LUMOs of sixteen different structures from three different groups were analyzed. The energy differences between the HOMOs and LUMOs of the various unsymmetrical *trans*-stilbenes are in accord with the maximum absorption peaks of the experimental UV spectra of **1-3**. The calculated normal vibrational modes of **2l** were comparable with its experimental IR spectrum. The π-conjugation in the *para*-connected biphenyl group of **2** is better than the one in the *meta*-connected biphenyl group on the shorter side of **3**.

Key Words: *m*PW1PW91, Gibbs free energies, HOMO and LUMO, UV Spectrum, *trans*-Stilbene

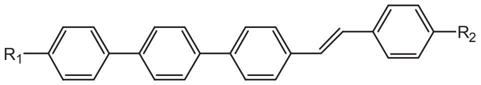
Introduction

Stilbene derivatives' biological[1] and optical[2] properties give them many potential applications. They have been extensively studied as prototypes for photochemical *cis-trans* isomerization of 1,2-disubstituted olefins[2b,c] and as short subunits of poly (*p*-phenylenevinylene), the first light-emitting polymer for organic light-emitting diodes (OLEDs).[3] The development of better luminophores could be aided by a better comprehension of the light emission mechanism and, as such, a systematic study of the relationship between the compound's structure and its emitted light.[4] Commercial OLEDs require stable organic luminescent materials of high quantum efficiency. The unsymmetrical *trans*-stilbenes (**1-3**) in Schemes 1-3 are promising groups of organic blue luminescent materials. Recently, their liquid[5a]- and solid[5b]-phase syntheses and their absorption and emission specifications have been published.

This paper reports total electronic energies, normal vibrational modes, Gibbs free energies, dipole moments, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies of the *trans*-stilbene compounds (**1-3**) calculated by the *m*PW1PW91/6-311G(d,p). Also compared are the calculated gaps between their HOMOs and LUMOs and the λ_{max} values from their experimental UV spectra.

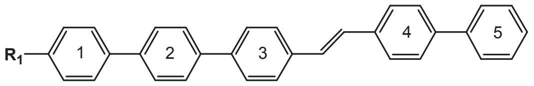
Computational Methods

The initial conformations of **1-3** were constructed by using the molecular mechanics (MM), molecular dynamics (MD), and semi-empirical calculations of HyperChem.[6] Optimized structures were found by conformational searches by a previously described simulated annealing method.[7] The structures of **1-3** obtained from the MM/MD and AM1/PM3 calculations were fully re-optimized using an *m*PW1PW91 method to determine both the relative energies and structures of sixteen distinct structures. Modified Perdew-Wang 1-parameter (*m*PW1)



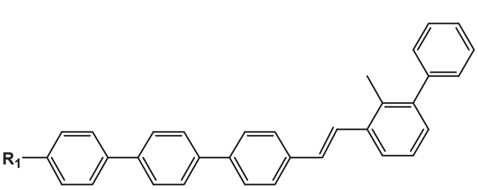
	R_1	R_2
1a	H	H
1b	CH_3	H
1c	*t*-Bu	H
1d	H	CH_3
1e	CH_3	CH_3
1f	*t*-Bu	CH_3
1g	H	*t*-Bu
1h	CH_3	*t*-Bu
1i	*t*-Bu	*t*-Bu

Scheme 1. Various unsymmetrical *trans*-stilbene derivatives **1**



	R_1
2j	H
2k	CH_3
2l	*t*-Bu

Scheme 2. Three unsymmetrical *trans*-stilbene derivatives **2**



	R_1
3m	CH_3
3n	*t*-Bu

Scheme 3. Two unsymmetrical *trans*-stilbene derivatives **3**

calculation methods,[8,9] such as *m*PW1PW91, are new hybrid Hartree-Fock-density functional (HF-DF) models which obtain remarkable results both for covalent and non-covalent interactions.[8] The *m*PW1PW91/6-311G(d,p) method was used to calculate the normal mode frequencies of the final structures. Each vibrational spectrum shows no negative frequencies, confirming that the optimized structures exist in energy minima. For direct comparison with experimental data, the calculated frequencies were scaled by the recommended scale factor.[10] Furthermore, broadened IR spectra are presented assuming a Lorentzian line width of 10 cm^{-1}. Additional *m*PW1PW91/6-311+G(d,p) optimizations were performed using Gaussian 03 to obtain their total electronic, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies.[11]

Table 1. *m*PW1PW91/6-311G(d,p) calculated total electronic and Gibbs free energies, dipole moments and first vibrational frequencies of the normal modes (ν_1) of **1**-**3**

Compound	Total Electronic Energy[a]	Gibbs Energy at 298 K[b]	Dipole Moment[c]	ν_1[d]
	(a.u.)	(a.u.)	Debye	cm^{-1}
1a	−1002.80865	−1002.48353	0.0327	14.33350
1b	−1042.12702	−1041.77768	0.6484	14.03000
1c	−1160.06818	−1159.63722	0.6441	12.05720
1d	−1042.12718	−1041.77752	0.7004	12.75150
1e	−1081.44554	−1081.07013	0.0994	8.94190
1f	−1199.38670	−1198.93078	0.0912	10.43110
1g	−1160.06827	−1159.62248	0.6044	22.97570
1h	−1199.38662	−1198.93365	0.1029	3.32080
1i	−1317.32780	−1316.79069	0.0789	9.20730
2j	−1233.86281	−1233.46333	0.0162	9.48880
2k	−1273.18119	−1272.76031	0.6358	1.66410
2l	−1391.12236	−1390.61631	0.6289	10.24390
3m	−1312.49217	−1312.04094	0.8782	16.18000
3n	−1430.43364	−1429.90149	0.8505	11.18250

[a]Error limit is about 0.00001 a.u. [b]Sum of electronic and thermal Gibbs free energies at 298 K including zero-point energies. [c]Total dipole moment of the optimized structure. [d]The first vibrational frequencies of the calculated normal modes.

Result and Discussion

The various unsymmetrical *trans*-stilbene derivatives have been assigned to one of three categories. All three categories have terphenyl moiety on the longer side in common, but different phenyl groups on the shorter side. The first (**1a-1i**) has a single phenyl ring, the second (**2j-2l**) has a para-biphenyl group, and the third (**3m-3n**) has a meta-biphenyl group on the shorter side.

Molecular structures of the unsymmetrical *trans*-stilbene derivatives (**1-3**) were optimized by *m*PW1PW91/6-311G(d,p) and *m*PW1PW91/6-311+G(d,p). The total electronic energies, Gibbs free energies, dipole moments, normal vibrational frequencies and the HOMOs (highest occupied molecular orbital) and LUMOs (lowest unoccupied molecular orbital) of sixteen different structures from the three groups were analyzed.

Table 1 reports the *m*PW1PW91/6-311G(d,p) optimized total

Table 2. *m*PW1PW91/6-311+G(d,p) calculated total electronic, HOMO and LUMO energies,[a] and the comparison of Δ(LUMO-HOMO) and λ_{max} from experimental UV spectra

	Calculated[a]							Experimental[c]
Entry[b]	Total Electronic	HOMO	LUMO	Δ(LUMO-HOMO)		Δ(LUMO-HOMO)		λ_{abs}
	(a.u.)	(a.u.)	(a.u.)	(a.u.)	J/mole	Wavelength (nm)	Scaled[d] Wavelength (nm)	Wavelength (nm)
1a	−1002.81759	−0.21682	−0.06699	0.14983	393397.21	304.09	331.61	327.0
1b	−1042.13605	−0.21524	−0.06587	0.14937	392189.43	305.02	332.63	333.0
1c	−1160.07747	−0.21508	−0.06592	0.14916	391638.05	305.45	333.10	333.0
1d	−1042.13618	−0.21273	−0.06465	0.14808	388802.37	307.68	335.53	336.0
1e	−1081.45457	−0.21174	−0.06315	0.14859	390141.44	306.62	334.38	335.0
1f	−1199.39604	−0.21143	−0.06328	0.14815	388986.17	307.53	335.37	336.0
1g	−1160.07757	−0.21280	−0.06450	0.14830	389380.01	307.22	335.03	335.0
1h	−1199.39602	−0.21145	−0.06337	0.14808	388802.37	307.68	335.53	335.0
1i	−1317.33744	−0.21133	−0.06338	0.14795	388461.04	307.95	335.82	339.0
2j	−1233.87368	−0.21362	−0.07012	0.14350	376777.02	317.50	346.24	346.5
2k	−1273.19212	−0.21229	−0.06912	0.14317	375910.56	318.23	347.04	347.0
2l	−1391.13359	−0.21224	−0.06904	0.14320	375989.33	318.17	346.96	344.0
3m	−1312.50376	−0.21599	−0.06367	0.15232	399935.02	299.12	326.19	329.5
3n	−1430.44523	−0.21601	−0.06346	0.15255	400538.91	298.66	325.70	329.0

[a]Error limit is about 0.00001 a.u. [b]See Schemes 1-3 for the list of the compounds. [c]λ_{abs} represents the maximum absorption wavelength. λ_{abs} values of **1a-1i** compounds were already published,[5b] and the values of **2** and **3** are obtained from the same experimental condition (in chloroform) as **1** in our laboratory.[†] [d]The calculated wavelength scaled by division by 0.910, to adjust it for favorable comparison with experimental observations.[10] This value (0.910) is an optimized parameter so that best agreement between experiment and theory is obtained.

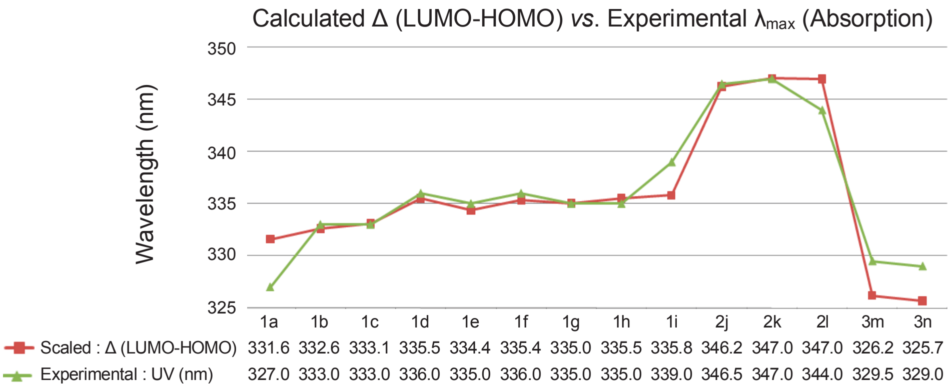


Chart 1. Comparison of calculated Δ(LUMO-HOMO) and the experimental maximum absorption wavelength (λ_{max}) of the UV spectra of **1-3** from the data of Table 2.

Table 3. Main features of *m*PW1PW91/6-311G(d,p) calculated normal vibrational modes and experimental IR peaks of a *trans*-Stilbene (**2l**)

Calculated			Normal vibrational modes			Experimental
Normal mode #	Frequency (wave number)	Scaled[a] (0.92)	Intensity	Vibrational motions	Phenyl ring[b] (see Scheme 2)	Peak assignment (wave number)
45	543	500	21	C-H waggings (out-of plane) in benzene rings	(#3 and #5)	513
47	564	520	26		(#1 ~ 5)	571
57	719	664	39		(#5)	690
64	786	724	33		(#3 ~ 5)	725
69	852	784	74		(#1 ~ 4)	766
95	1021	940	42	C-C-C bendings in benzene rings	(#1 ~ 3)	814
106	1142	1051	39		(#1)	1103
121	1304	1199	47	C-C stretching between *t*-butyl and a benzene ring	(#1)	1263
152	1538	1415	192	C-H waggings (in plane) and C-C stretchings in benzene rings	(#1 ~ 3)	1462
162	1671	1535	18	C-C stretchings in benzene ring	(#5)	1668
169	3052	2805	78	C-H symmetric stretchings in *t*-butyl group		2852
172	3125	2877	138	C-H anti-symmetric stretchings in *t*-butyl group		2922
177	3173	2933	102	C-H anti-symmetric stretchings in -CH=CH- group		2954
179	3184	2953	79	C-H anti-symmetric stretchings in a benzene ring	(#4)	2964

[a]The calculated frequency is scaled by multiplication by 0.920, adjusted it for favorable to comparison with experimental observations.[10] [b]Phenyl ring # which has stronger vibrational motion. (See Scheme 2 for the numbering of phenyl group.)

electronic and Gibbs free energies and dipole moments of the sixteen compounds. Their normal vibrational modes were analyzed, and their first vibrational frequencies (ν_1) are also listed in Table 1. None of these frequencies are negative, confirming that the optimized structures exist in energy minima.

Table 2 reports total electronic, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies of the sixteen structures calculated by mPW1PW91/6-311+G(d,p) (hybrid HF-DF). The wavelength differences between HOMOs and LUMOs were divided by 0.910 to adjust the calculated values so that they compare favorably with experimental observations.[10] Experimental UV absorptions, λ_{max}, of solid-state stilbenes are also shown in Table 2.

Chart 1 shows how the calculated LUMO-HOMO differences favorably compare to experimental UV absorptions, λ_{max}. The elevated values for the compounds (**2j-2l**) in Chart 1 are caused by the additional π-conjugation of the π-electrons in the para-connected biphenyl group (phenyl rings #4 and #5 of Scheme 2) on the shorter side of the unsymmetrical *trans*-stilbene derivatives. However no extra π-conjugation is possible in the meta-connected biphenyl groups of **3m-3n** and in the single phenyl groups of the **1a-1i** compounds. These characteristic differences are well reproduced in the *m*PW1PW91/6-311+G(d,p) calculated values.

Table 3 compares **2l**'s normal vibrational modes calculated by *m*PW1PW91/6-311G(d,p) with the intensities of prominent peaks in its experimental IR spectrum. Also listed are the assignments of the experimental peaks compared with the calculated values in Table 3.

Figures 4 and 5 show the calculated and experimental IR

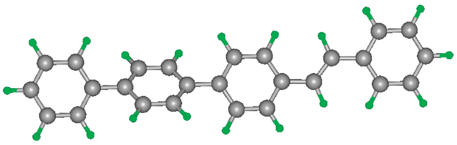
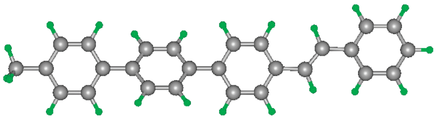
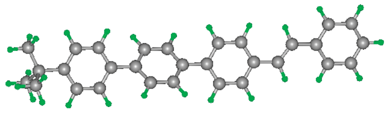
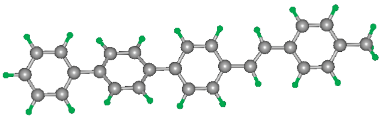
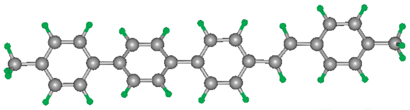
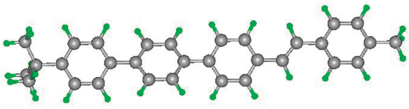
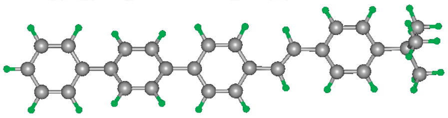
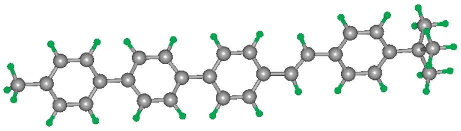
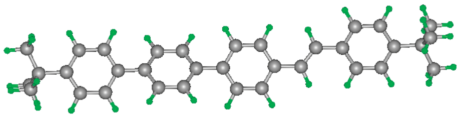
Entry	Optimized structure
1a	
1b	
1c	
1d	
1e	
1f	
1g	
1h	
1i	

Figure 1. The *m*PW1PW91/6-311+G(d,p) calculated nine unsymmetrical *trans*-stilbene derivatives of **1**. The first category (**1a-1i**) has single phenyl ring on the shorter side and three phenyl rings on the longer moiety. The visualization of the optimized structures in Figures 1-3 was performed with PosMol.[12]

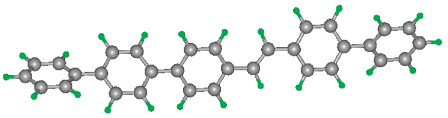
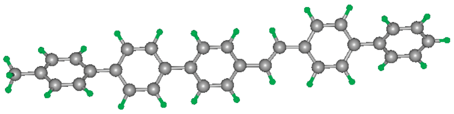
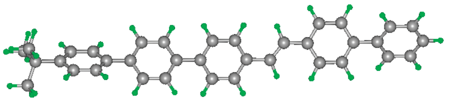
Entry	Optimized structure
2j	
2k	
2l	

Figure 2. The *m*PW1PW91/6-311+G(d,p) calculated three *trans*-stilbene derivatives of **2**. The second category (**2j-2l**) case has a para-biphenyl group on the shorter side and three phenyl rings on the longer moiety.

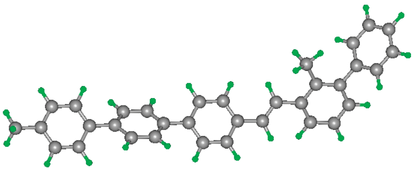
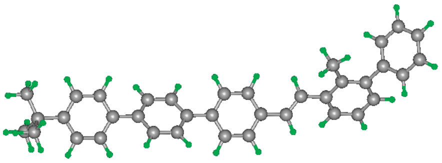
Entry	Optimized structure
3m	
3n	

Figure 3. The *m*PW1PW91/6-311+G(d,p) calculated two *trans*-stilbene derivatives of **3**. The third category (**3m-3n**) has a meta-biphenyl group on the shorter side and three phenyl rings on the longer moiety.

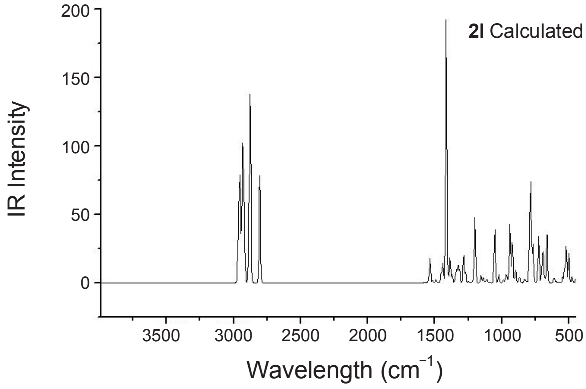


Figure 4. The *m*PW1PW91/6-311G(d,p) calculated IR spectrum of **2l**.

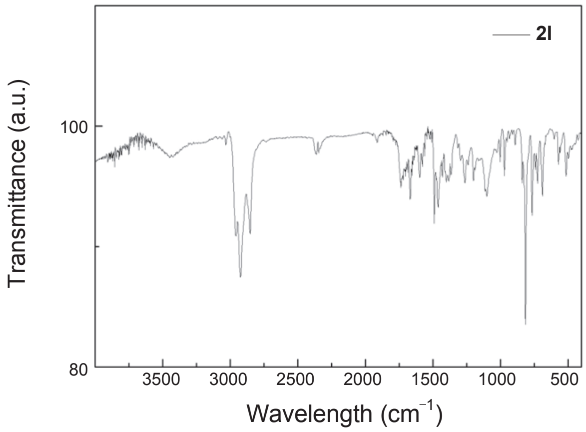


Figure 5. The experimental IR spectrum of **2l**.

spectra of **2l**, respectively. Most of the frequencies and intensities of the calculated normal modes are in accord with the experimental IR peaks. However, some of intensities are not; especially #95 (C-C-C bending) and #152(C-C stretching) normal vibrational modes.

Conclusions

The total electronic energies, normal vibrational modes, Gibbs free energies, dipole moments, and HOMOs (highest occupied molecular orbital) and LUMOs (lowest unoccupied molecular orbital) of sixteen different structures from three different groups of *trans*-stilbene derivatives were calculated using *m*PW1PW91/6-311G(d,p). Their calculated gaps between the HOMOs and LUMOs are in excellent agreements with their maximum absorption peaks in experimental UV spectra. Most of the frequencies and intensities of the calculated normal modes of **2l** favorably agree with its experimental IR peaks.

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