Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 133 (2014) 307–317

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Structural investigation of a self-assembled monolayer material 5-[(3-methylphenyl) (phenyl) amino] isophthalic acid for organic light-emitting devices

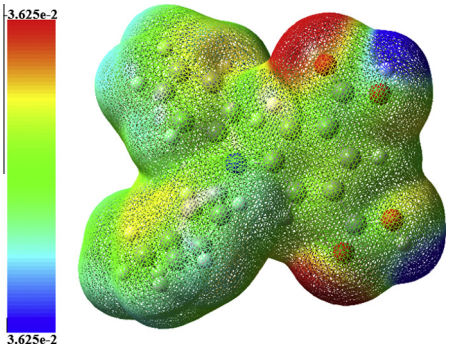
E. Babur Saş [a], M. Kurt [a,*], M. Can [b], S. Okur [c], S. İçli [d], S. Demiç [c]

[a] Department of Physics, Ahi Evran University, Kırsehir, Turkey
[b] Department of Engineering Sciences, Faculty of Engineering, Izmir Katip Celebi University, Cigli, 35620 Izmir, Turkey
[c] Izmir Katip Çelebi University, Material Science and Engineering, Çiğli, Izmir, Turkey
[d] Ege University, Solar Energy Institute, 35040 Bornova, Izmir, Turkey

HIGHLIGHTS

- Molecular structure of 5-[(3-methylphenyl) (phenyl) amino] isophthalic acid was studied.
- The FT-IR, Raman, NMR and UV–vis spectra of studied molecule were compared with calculated spectra.
- The vibrational frequencies were calculated by DFT method and discussed.
- The complete assignments are performed on the basis of the potential energy distribution (PED).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 March 2014
Received in revised form 1 May 2014
Accepted 9 May 2014
Available online 20 May 2014

Keywords:
5-[(3-Methylphenyl) (phenyl) amino] isophthalic acid (MePIFA)
DFT
FT-IR
FT-Raman
Dispersive Raman
UV and NMR spectra

ABSTRACT

The molecular structure and vibrations of 5-[(3-methylphenyl) (phenyl) amino] isophthalic acid (MePIFA) were investigated by infrared and Raman spectroscopies, UV–Vis, ^{1}H and ^{13}C NMR spectroscopic techniques and NBO analysis. FT-IR, FT-Raman and dispersive Raman spectra were recorded in the solid phase. ^{1}H and ^{13}C NMR spectra and UV–Vis spectrum were recorded in DMSO solution. HOMO–LUMO analysis and molecular electrostatic potential (MEP) analysis were performed. The theoretical calculations for the molecular structure and spectroscopies were performed with DFT (B3LYP) and 6-311G(d,p) basis set calculations using the Gaussian 09 program. After the geometry of the molecule was optimized, vibration wavenumbers and fundamental vibration wavenumbers were assigned on the basis of the potential energy distribution (PED) of the vibrational modes calculated with VEDA 4 program. The total (TDOS), partial (PDOS) density of state and overlap population density of state (OPDOS) diagrams analysis were made using GaussSum 2.2 program. The results of theoretical calculations for the spectra of the title compound were compared with the observed spectra.

Introduction

TPD known as a triarylamine compound with two triphenylamine (TPA) moieties is widely used in organic light-emitting diodes (OLEDs) as hole-transport material [1–10]. The structure of

* Corresponding author. Tel.: +90 386 280 45 25; fax: +90 386 252 80 54.
E-mail address: kurt@gazi.edu.tr (M. Kurt).

http://dx.doi.org/10.1016/j.saa.2014.05.021
1386-1425/

TPA molecules with nitrogen atom is planar. This means, that the nitrogen atom and the three carbon atoms covalently bonded to the nitrogen atom are in the same plane [11–17]. The development of organic light-emitting diodes (OLEDs) has progressed due to their potential applications in many fields [16–18]. Multilayer OLEDs are known as one of the potential technologies for the next generation flat-panel display devices [18,19]. Multilayer OLED are fabricated as sandwich like structures between an indium tin oxide (ITO) anode and a metal cathode with an electron-transporting material (ETM) layer, a hole-transporting material (HTM) layer inside [18].

In this work, the spectroscopic approach of 5-[(3-methylphenyl) (phenyl) amino] isophthalic acid (MePIFA) molecule was investigated. The structure of molecule was optimized with DFT/B3LYP 6-311G(d,p). Infrared and Raman spectra were calculated and vibrational assignments were performed based upon potential energy distributions (PED). NMR and UV absorption spectra were recorded and compared with theoretically obtained spectra in DMSO. Additionally, HOMO LUMO and natural bond orbital (NBO) analysis were also carried out for MePIFA by DFT. Besides the total density of states (TDOS or DOS), the partial density of states (PDOS) and overlap population density of states (OPDOS) spectra of molecule were calculated using GaussSum 2.2 [20].

Experimental

The title compound was synthesized for the first time by Okur et al. [21]. The compound MePIFA in solid form were prepared using a KBr disc technique. The infrared spectrum of the compound was recorded in the range of 4000–600 cm^{-1} on a Perkin–Elmer FT-IR system spectrum BX spectrometer. The spectrum was recorded at room temperature, with a scanning speed of 10 cm^{-1} min^{-1} and the spectral resolution of 4.0 cm^{-1}. The Raman spectra of the compound were recorded between 3500–40 cm^{-1} with a Thermo Fisher Scientific model DXR dispersive Raman instrument using 532 and 780 nm laser excitation. FT-Raman spectrum of MePIFA did not provide any spectra. An InGaAs detector was used at room temperature. One hundred scans were collected with 4 cm^{-1} resolution by using a laser power of 100 mW. The ultraviolet absorption spectra of sample solved in DMSO was examined between 200 nm and 1100 nm with resolution of 1 nm by using Princeton Instrument Model of Acton Advanced SP2300A with two monochromator, UV–Vis recording spectrometer. The sample spectrum was taken inside a quartz tupe with DMSO. NMR experiments were performed in Bruker at 300 K. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for ^1H and

Table 1
Same selected vibrational frequencies of MePIFA molecule.

No	Experimental wavenumber			Theoretical wavenumber				PED[a] (⩾10%)
	FT-IR	Dispersive Raman		Scaled[b]	I_{IR}	S_{Ra}	I_{Ra}	Assignments
		532 nm	780 nm					
9			63w	61	0.51	7.60	52.33	δCCN(39) + ΓCCCC(21)
10			86m	122	0.46	0.45	0.88	δCCC(67)
15			214w	206	3.78	4.71	3.68	ΓCCCC(55) + ΓCCCH(11) + ΓCCNC(15)
16		221w		230	1.96	6.80	4.40	δCCN(22) + ΓCCCC(51) + ΓCCNC(11)
21		333vw		340	3.68	5.16	1.80	υCC(48) + δCCC(22) + δOCO(18)
34				591	1.95	7.98	1.23	γOH[ΓCCOH(85)]
39	642vw	640vw		636	47.52	7.84	1.08	δCCC(35) + ΓCCCC(16) + γOH[ΓCCOH(11)]
43	696m	702vw		693	37.07	2.66	0.32	ΓCCCC(34) + ΓCCCH(28) + ΓCCNC(16)
46	758w			759	19.70	1.14	0.12	ΓCCCC(28) + ΓCCCH(30) + ΓCNCH(19)
48			776vw	776	4.90	3.41	0.35	ΓCCCC(11) + ΓCCCH(41) + ΓOCOC(19)
55	902vw			905	2.16	0.12	0.01	ΓCCCC(20) + γCH[ΓCCCH(73)]
57	935vw			930	0.84	2.93	0.23	γCH[ΓCCCH(77)]
60			950vw	952	0.10	0.23	0.02	ΓCCCC(20) + γCH[ΓCCCH(79)]
65			994m	983	12.63	36.65	2.66	υCC(26) + δCCC(59)
66		998vs		1007	72.10	5.77	0.41	υCC(18) + δCCC(27) + δCCH(10) + ΓCCCH(16)
69		1060vw		1069	9.38	1.05	0.07	υCC(45) + δCH[δCCH(44)]
78	1166vw			1164	184.96	22.86	1.29	υCC(30) + δCH[δCCH(18)] + δCOH(24)
79		1218vw		1206	48.77	125.46	6.72	υCC(34) + υCN(20) + δCCC(12) + δCH[δCCH(13)]
80				1238	40.18	19.22	0.99	υCC(19) + δCH[δCCH(63)]
81				1255	36.60	49.19	2.47	υCC(50) + υCN(14) + δCH[δCCH(22)]
83	1273vs			1279	77.91	72.76	3.55	υCC(27) + υCN(24) + δCCC(11) + δCCH(30)
84		1292vw		1289	29.17	28.52	1.37	υCC(52) + υCN(11) + δCCH(17)
88	1321m			1316	45.59	19.83	0.93	υCO(14) + δOCO(12) + δOH[δCOH(33)]
89		1340vw		1354	487.22	79.57	3.55	υCC(28) + υCO(14) + δCCC(12) + δOCO(10) + δCOH(20)
93	1428m			1429	37.32	4.88	0.20	υCC(48) + δCCC(10) + δCCH(26)
94				1441	16.18	2.78	0.11	υCC(32) + δCCC(11) + ρCH[δCCH(40)]
95				1442	7.76	13.76	0.55	ρCH[δHCH(53)] + ΓCCCH(14)
96	1452m			1452	18.56	2.76	0.11	υCC(14) + δCCH(12) + δHCH(53) + ΓCCCH(14)
98	1493m			1474	110.92	15.70	0.61	υCC(14) + δCCC(18) + δCCH(58)
103	1587s		1586w	1585	64.59	98.52	3.36	υCC(61) + δCCC(17) + δCCH(16)
104		1594m		1593	13.70	145.90	4.94	υCC(46) + δCCC(16) + δCCH(18)
105	1688vs			1742	509.80	21.19	0.61	υCO(84)
106		2027vw	2230w	1747	56.13	122.68	3.50	υCO(84)
107	2656w	2918vw		2924	29.38	231.36	2.03	υCH(100)
108	2863w			2977	18.66	84.25	0.70	υCH(99)
109				3002	16.98	71.89	0.59	υCH(100)
110				3058	4.61	78.56	0.61	υCH(100)
111	3033w	3061vw		3060	3.45	35.34	0.27	υCH(100)
121			3185vw	3135	5.97	50.88	0.37	υCH(100)
122	3633vw		3380vw	3647	114.08	193.68	0.86	υOH(100)
123				3648	93.21	242.02	1.08	υOH(100)

[a] PED: potential energy distribution, ν; stretching, γ; out-of plane bending, δ; in-plane bending, τ; torsion, ρ; scissoring, φ; twisting, r; rocking.
[b] Scaling factor was used as 0.967.