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DFT, *Ab initio* and FT-IR Studies of the Structure of Sulfonamide Triazenes

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We present an in-depth investigation of the structural, infrared spectra and visible spectra of various triazenes with a sulfonamide moiety. The preparation of 4-sulfonyl amide benzenediazonium chloride with cyclic amines of various ring sizes (pyrrolidine, piperidine, 4-methylpiperidine, N-methylpiperazine, morpholine and hexamethyleneimine) are theoretically investigated using the density functional theory (DFT) and Hartree-Fock (HF) levels of theory with the standard 6-31G* basis set. The calculated vibrational frequencies are evaluated *via* comparison with experimental values. The vibrational spectral data obtained from solid-phase FT-IR spectra are assigned modes based on the results of the theoretical calculations. The UV-Vis spectrum of each compound is measured in various solvents with a wide range of polarity to examine the role of solvent chemistry on observed spectral changes. The calculated spectra are in good agreement with the experimental spectra.

Keywords: Triazenes, Sulfonamide, Vibrational frequencies, Visible, DFT, *Ab initio*

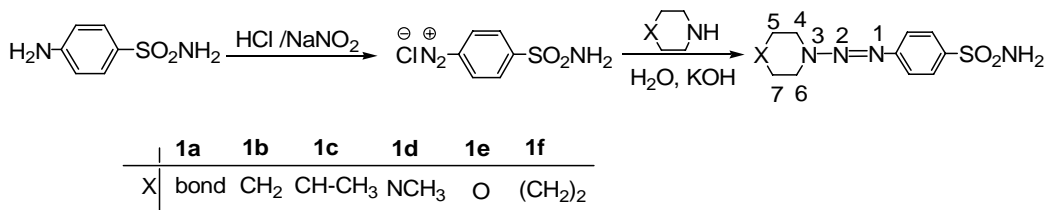
INTRODUCTION

Triazenes are a group of organic compounds synthesized by diazotization of an aromatic primary amine, followed by coupling of the diazonium salt to a secondary amine to provide the desired triazene [1]. Useful to scientists in pharmacology, total synthesis, polymer technology, and the construction of novel ring systems, aryl triazenes are of considerable interest for their reported biological activities, and have found use in cancer therapy [2], in addition to their other notable properties. The importance of triazenes as versatile tools in organic synthesis has also been reviewed recently [3]. Triazenes [4] and chemical compounds with benzenesulfonamide groups have interesting biological properties and potential applications as drugs [5]. Previous theoretical studies on triazene systems have been reported

[6]. A dynamic NMR study of triazenes was first described by Lunazzi *et al.* [7] and then another by Limbach *et al.* [8]. Kimball *et al.* studied the mechanistic aspects of the cyclization of a group of dialkyltriazenes using a variety of methods, including density functional theory (DFT) and basis sets [9]. Theoretical studies of the molecular conformations and properties of benzene-sulfonamides [10], sulfonamide-substituted systems [11], and aromatic and heterocyclic sulfonamide compounds have been performed [12]. More convenient methods for the synthesis of novel compounds of this class are highly desirable.

We have recently reported the DFT calculation of the 4-substituted aminoazo-benzenesulfonyl azides [13] and a series of azo dyes derived from 2-hydroxy and 2,4-dihydroxy benzoic acids [14]. The present work aims at rationalizing and predicting with accuracy the frequency of the vibrational bands and absorption maxima (λ_{\max}) of a series of 4-substituted aminoazo-benzenesulfonyl amides with cyclic amines of various ring sizes

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Scheme 1. Chemical structure of prepared triazenes

(pyrrolidine, piperidine, 4-methylpiperidine, N-methylpiperazine, morpholine and hexamethylenimine) recently synthesized by our group [15].

EXPERIMENTAL

Synthesis

Triazenes **1a-1f** were synthesized as previously published [15]. FT-IR spectra of the triazenes were recorded using the KBr technique, in the region 4000-400 cm⁻¹ and calibrated with polystyrene. Spectra were recorded with a JASCO FT/IR-680 PLUS spectrometer. The UV-Vis spectra were measured with a Shimadzu UV 160A spectrophotometer. The solvents used were of spectrophotometric grade, purchased from Merck and Aldrich and used as received.

Computational Analysis

The molecular structures of 4-substituted aminoazo-benzenesulfonyl azides in the ground state were optimized with HF and Becke 3-Lee-Yang-Parr (B3LYP) functionals [16,17], by means of visual inspection using the Gauss view program [18], supplemented with the standard 6-31G* basis set (referred to as DFT calculations). The vibrational frequencies and the visible absorption maxima were also calculated with these methods. These calculations were carried out using the Gaussian 98 software package [19]. Initial geometries were obtained with the PM3 method based on the Hyperchem 6 package [20]. The convergence was set to 0.001 kcal mol⁻¹. Vibrational frequencies for these species are calculated using these methods and then scaled by factors of 0.8991 and 0.9663 for HF/6-31G* and B3LYP/6-31G* [21].

RESULTS AND DISCUSSION

Molecular Structure of Triazenes

The general route for the synthesis of triazene, previously reported [15], is shown in Scheme 1. In the present study, we report the DFT(B3LYP)/HF calculation results for these triazenes in order to give their optimal molecular geometry and vibrational modes. Here, we focus on the use of modern density functional theory to fully account for the experimental vibrational IR data for triazenes **1a-1f**.

The optimized configurations are shown in Fig. 1. The geometric optimization yields the chair conformation for six-member skeletons and half-chair conformation for cyclopentane. The most stable conformations are the twist-chair for cycloheptane and planar for the benzene ring.

The DFT calculated geometric parameters for triazenes **1a-1f** are compared in Table 1. The reference compounds used for comparison are 1-aryl-3,3-dimethyltriazenes [22-24]. The bond lengths calculated for compounds **1a-1f** for Csp²-N at the HF level range from 1.412 to 1.415 Å, at the B3LYP level from 1.410 to 1.414 Å, and those of the references range from 1.415 to 1.433 Å. The bond lengths calculated for N1=N2 for compounds **1a-1f** at the HF level range from 1.225 to 1.234 Å, at the B3LYP level from 1.270 to 1.272 Å, and those of the references range from 1.270 to 1.282 Å. The bond lengths calculated for N2-N3 for compounds **1a-1f** at the HF level range from 1.297 to 1.325 Å, at the B3LYP level from 1.303 to 1.329 Å, and those of the references range from 1.282 to 1.307 Å.

The calculations of the total energies, relative energies of the optimized structures, dipole moments and relative dipole moments at HF and B3LYP levels are presented in Table 2. The energy ratios (kcal) and dipole moments (Debye) indicate the consistency between the two calculation methods (DFT/HF).

Assignments of Vibrational Frequencies

Vibrational spectroscopy is used extensively in organic chemistry for the identification of functional groups of organic compounds as well as studies on molecular conformation and

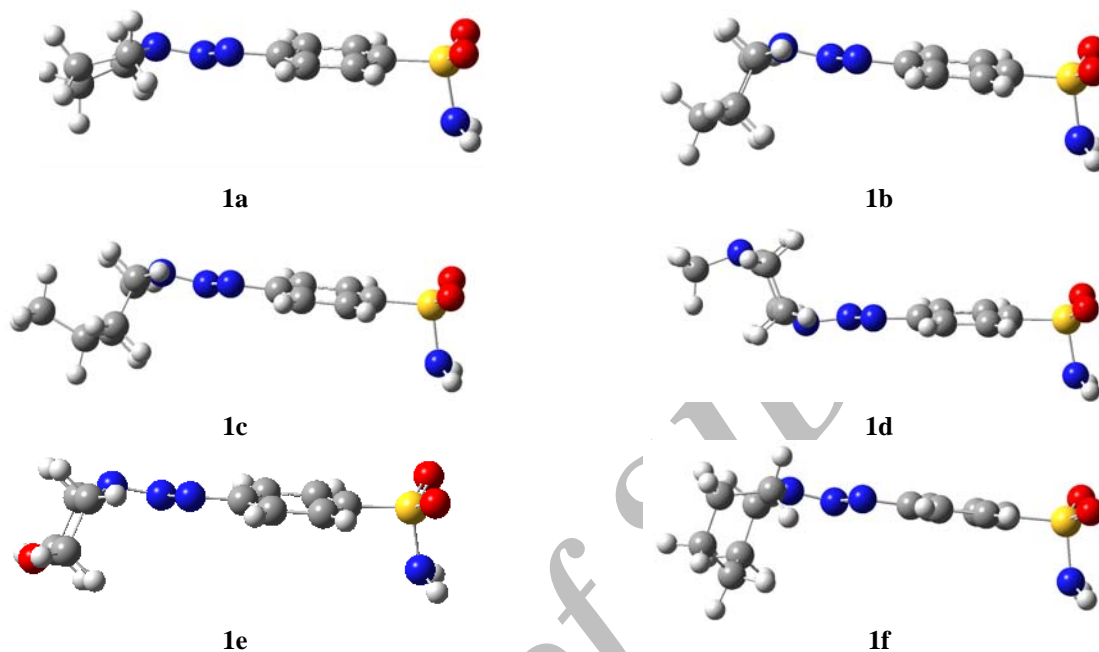


Fig. 1. The structures of triazenes **1a-1f**. Optimizations were performed by the B3LYP/6-31G* method.

Table 1. Selected Bond Distances (Å), Bond Angles (°) and Torsional Angles (°) of 6-31G* Optimized Triazenes

Entry	HF/6-31 (B3LYP/6-31)					
	1a	1b	1c	1d	1e	1f
C _{sp2} -N ₁	1.4120 (1.4113)	1.4149 (1.4128)	1.4148 (1.4127)	1.4149 (1.4108)	1.4159 (1.4140)	1.4125 (1.4123)
N ₁ =N ₂	1.2344 (1.2774)	1.2270 (1.2707)	1.2272 (1.2711)	1.2271 (1.2721)	1.2254 (1.2688)	1.2339 (1.2755)
N ₂ -N ₃	1.2965 (1.3126)	1.3213 (1.3304)	1.3211 (1.3297)	1.3215 (1.3273)	1.3254 (1.3335)	1.3037 (1.3230)
N ₃ -N ₂ =N ₁	115.5 (113.8)	117.0 (115.4)	117.0 (115.3)	117.0 (115.5)	116.9 (114.9)	116.1 (114.4)
N ₂ -N ₃ -C ₆	125.0 (125.3)	121.9 (123.2)	121.9 (123.1)	122.0 (124.8)	122.0 (123.0)	120.7 (121.1)
N ₂ -N ₃ -C ₄	120.2 (120.4)	113.9 (115.0)	114.0 (115.0)	114.1 (116.7)	114.1 (115.3)	116.0 (116.0)
N ₃ -C ₆ -C ₇	102.3 (102.3)	110.7 (110.2)	110.6 (110.2)	109.6 (109.1)	109.5 (108.8)	112.5 (112.8)
N ₃ -C ₄ -C ₅	102.3 (102.7)	111.1 (110.7)	111.0 (110.7)	110.1 (109.7)	110.0 (109.1)	113.7 (113.7)
N ₂ -N ₃ -C ₆ -C ₇	173.8 (176.2)	-88.3 (-151.4)	-88.0 (-151.8)	90.5 (112.9)	-90.6 (-157.5)	-176.6 (-178.5)
N ₂ -N ₃ -C ₄ -C ₅	163.3 (161.2)	91.8 (148.2)	91.4 (148.7)	-93.8 (-114.0)	-52.2 (154.1)	107.7 (107.7)
N ₁ =N ₂ -N ₃ -C ₆	0.1 (-1.1)	-14.7 (7.2)	-15.0 (6.8)	15.4 (7.0)	-15.9 (9.0)	0.1 (0.6)
N ₁ =N ₂ -N ₃ -C ₄	-179.1 (-179.0)	-160.1 (165.2)	-160.1 (165.1)	160.0 (171.1)	-159.0 (163.5)	179.3 (-179.2)

reaction kinetics, among others. Assignments for complex systems can be proposed on the basis of frequency agreement between the computed harmonics and the observed fundamentals.

The resulting vibrational wave numbers for the optimized geometry and the experimental wave numbers together with the proposed assignments are given in Table 3. The vibrational

Table 2. The Total and Relative Energies and Dipole Moments of Triazenes **1a-1f**

	HF/6-31G*		B3LYP/6-31G*		Energy ratio ^b (B3LYP/HF)	μ (B3LYP/HF)
	Total energy ^a	μ	Total energy ^a	μ		
1a	-1151.7285738	7.5011	-1157.0192558	7.5898	630.392	1.01
1b	-1190.7653107	6.9957	-1196.3373097	6.9269	630.446	0.99
1c	-1229.7974521	7.0749	-1235.6492742	7.0431	630.495	0.99
1d	-1245.7692872	6.2826	-1251.6663036	6.9031	630.480	1.09
1e	-1226.5720794	5.1766	-1232.2248590	5.4088	630.401	1.00
1f	-1229.8795423	7.4304	-1235.6414618	7.5958	630.495	1.02

^aTotal energy in Hartree units and energy ratio in kcal. ^b μ = total dipole moment.

Table 3. Calculated and Observed Vibrational Frequencies of 6-31G* Optimized Triazenes **1a-1f**

	1a			Assignment	1b			Assignment	1c			Assignment
	HF	B3LYP	Exp.		HF	B3LYP	Exp.		HF	B3LYP	Exp.	
1	3487	3662	3497	$\nu_{asym.}$ (NH ₂)	3484	3660	3496	$\nu_{asym.}$ (NH ₂)	3492	3656	3498	$\nu_{asym.}$ (NH ₂)
2	3392	3557	3416	$\nu_{sym.}$ (NH ₂)	3388	3554	3438	$\nu_{sym.}$ (NH ₂)	3395	3552	3443	$\nu_{sym.}$ (NH ₂)
3	2866	2988	3250	ν (CH)	2867	2989	3093	ν (CH)	2871	2987	3095	ν (CH)
4	2864	2985	3035	ν (CH)	2864	2985	2983	ν (CH)	2868	2985	2992	ν (CH)
5	2844	2965	2946	ν (CH)	2845	2966	2957	ν (CH)	2846	2967	2988	ν (CH)
6	2841	2960	2934	ν (CH)	-	-	1937	ν_{ring}	-	-	1999	$\nu_{asym.}$ (N ₃)
7	-	-	2044	$\nu_{asym.}$ (N ₃)	-	-	1793	ν_{ring}	-	-	1925	ν_{ring}
8	-	-	1826	ν_{ring}	-	-	1720	$\nu_{asym.}$ (N ₃)	-	-	1784	ν_{ring}
9	-	-	1725	ν_{ring}	1607	1608	1589	ν_{ring}	1607	1608	1699	ν_{ring}
10	1607	1608	1600	ν_{ring}	1579	1575	1577	ν (CH ₂)	1580	1574	1580	ν_{ring}
11	1499	1488	1486	ν_{ring}	1484	1468	1473	ν_{ring}	1483	1484	1498	ν_{ring}
12	1406	1480	1448	ν (CH ₂)	1371	1375	1385	$\nu_{asym.}$ (SO ₂)	1454	1464	1460	ν (CH ₂)
13	1359	1359	1360	$\nu_{asym.}$ (SO ₂)	1281	1280	1268	$\nu_{sym.}$ (N ₃)	1397	1388	1390	$\nu_{sym.}$ (N ₃)
14	1280	1280	1289	ν (CN)	1148	1124	1130	$\nu_{sym.}$ (SO ₂)	1346	1356	1357	$\nu_{sym.}$ (SO ₂)
15	1158	1180	1168	$\nu_{sym.}$ (SO ₂)	1091	1082	1087	ν (CN)	1260	1262	1261	ν (CN)
16	1104	1101	1108	ν (CN)	986	1000	998	π (CH)+ π (CN)	1183	1186	1178	ν (CN)
17	999	986	985	π (CH)+ π (CN)	938	950	939	π (SN)+ π (CH)	1093	1108	1112	$\nu_{sym.}$ (SO ₂)
18	937	959	957	π (SN)+ π (CH)	905	904	903	π (CS)+ π (CN)	1012	1013	1010	π (CH)+ π (CN)
19	903	911	910	π (CS)+ π (CN)	836	844	839	π , <i>para</i>	931	937	928	π (SN)+ π (CH)
20	844	858	859	π , <i>para</i>	758	745	769	δ_{ring}	891	885	893	π (CS)+ π (CN)
21	765	818	788	δ_{ring}	737	707	738	δ_{ring}	839	840	843	π , <i>para</i>
22	744	762	756	δ_{ring}	665	655	645	π (CS)+ π (CN)	761	746	752	δ_{ring}
23	632	680	669	π (CS)+ π (CN)	529	528	515	δ (SO ₂)	704	700	699	δ_{ring}
24	588	599	572	δ (SO ₂)	483	474	480	$\pi_{ring} + \omega$ (SO ₂)	628	634	628	π (CS)+ π (CN)
25	550	548	561	$\pi_{ring} + \omega$ (SO ₂)	-	-	-	-	492	493	507	δ (SO ₂)

Table 3. Continued

DFT, *Ab initio* and FT-IR Study of Structure of Sulfonamide Triazenes

	1d			Assignment	1e			Assignment	1f			Assignment
	HF	B3LYP	Exp.		HF	B3LYP	Exp.		HF	B3LYP	Exp.	
1	3483	3658	3488	$\nu_{asym.}(\text{NH}_2)$	3484	3660	3498	$\nu_{asym.}(\text{NH}_2)$	3546	3630	3485	$\nu_{asym.}(\text{NH}_2)$
2	3389	3554	3437	$\nu_{sym.}(\text{NH}_2)$	3389	3555	3442	$\nu_{sym.}(\text{NH}_2)$	3519	3504	3418	$\nu_{sym.}(\text{NH}_2)$
3	2871	2994	3069	$\nu(\text{CH})$	2867	2989	3072	$\nu(\text{CH})$	3181	3179	3066	$\nu(\text{CH})$
4	2864	2985	2982	$\nu(\text{CH})$	2865	2986	2980	$\nu(\text{CH})$	2975	2974	2988	$\nu(\text{CH})$
5	2847	2976	2967	$\nu(\text{CH})$	2845	2965	2968	$\nu(\text{CH})$	2952	2953	2949	$\nu(\text{CH})$
6	-	-	1918	ν_{ring}	-	-	2099	$\nu_{asym.}(\text{N}_3)$	1912	1911	1922	ν_{ring}
7	-	-	1764	ν_{ring}	-	-	1802	ν_{ring}	1768	1777	1783	ν_{ring}
8	1607	1609	1620	ν_{ring}	1608	1610	1744	ν_{ring}	1634	1626	1605	$\nu_{asym.}(\text{N}_3)$
9	1542	1560	1549	$\nu(\text{CH}_2)$	1579	1576	1570	ν_{ring}	1577	1579	1587	ν_{ring}
10	1454	1472	1468	ν_{ring}	1496	1484	1499	ν_{ring}	1445	1447	1440	ν_{ring}
11	1370	1372	1376	$\nu_{asym.}(\text{SO}_2)$	1440	1450	1436	$\nu(\text{CH}_2)$	1439	1434	1428	$\nu(\text{CH}_2)$
12	1260	1256	1262	$\nu_{sym.}(\text{N}_3)$	1252	1220	1233	$\nu(\text{CN})$	1410	1406	1399	$\nu_{sym.}(\text{N}_3)$
13	1150	1155	1150	$\nu_{sym.}(\text{SO}_2)$	1153	1157	1168	$\nu(\text{CN})$	1387	1385	1371	$\nu_{asym.}(\text{SO}_2)$
14	1093	1099	1083	$\nu(\text{CN})$	1135	1116	1113	$\nu_{asym.}(\text{CO})$	1263	1259	1286	$\nu(\text{CN})$
15	1012	1023	1015	$\pi(\text{CH})+\pi(\text{CN})$	1134	1109	1085	$\nu_{sym.}(\text{SO}_2)$	1169	1165	1139	$\nu(\text{CN})$
16	931	930	918	$\pi(\text{SN})+\pi(\text{CH})$	1092	1097	1115	$\pi(\text{CH})+\pi(\text{CN})$	1099	1092	1089	$\nu_{sym.}(\text{SO}_2)$
17	891	890	882	$\pi(\text{CS})+\pi(\text{CN})$	974	968	968	$\pi(\text{SN})+\pi(\text{CH})$	990	993	998	$\pi(\text{CH})+\pi(\text{CN})$
18	854	840	848	$\pi, para$	893	891	886	$\pi(\text{CS})+\pi(\text{CN})$	933	930	921	$\pi(\text{SN})+\pi(\text{CH})$
19	761	811	798	δ_{ring}	844	852	852	$\pi, para$	906	902	893	$\pi(\text{CS})+\pi(\text{CN})$
20	738	749	748	δ_{ring}	738	748	742	δ_{ring}	856	852	840	$\pi, para$
21	670	657	679	$\pi(\text{CS})+\pi(\text{CN})$	724	700	704	δ_{ring}	779	774	765	δ_{ring}
22	575	555	573	$\delta(\text{SO}_2)$	625	655	642	$\pi(\text{CS})+\pi(\text{CN})$	737	736	740	δ_{ring}
23	-	-	-	-	594	598	597	$\delta(\text{SO}_2)$	616	619	627	$\pi(\text{CS})+\pi(\text{CN})$
24	-	-	-	-	477	472	477	$\pi_{ring}+\omega(\text{SO}_2)$	521	518	486	$\delta(\text{SO}_2)$
25	-	-	-	-	-	-	-	-	459	455	469	$\pi_{ring}+\omega(\text{SO}_2)$

ν = stretching, δ = in-plane bending, π = out of plane bending, ω = wagging. Subscript: asym. = asymmetric, sym. = symmetric.

spectral data obtained from the solid-phase FT-IR spectra are assigned based on the results of the normal coordinate calculations. The observed and the calculated spectra reflect a reasonable agreement for the vibrational frequencies.

Based on comparisons of the calculated and experimental results, assignments of fundamental modes were examined. The assignment of the experimental frequencies incorporate the observed band frequencies in the infrared spectra of this species confirmed by establishing a one-to-one correlation between observed and theoretically calculated frequencies. The calculated frequencies are slightly higher than the observed values for the

majority of the normal modes. Many different factors may be responsible for the discrepancies between the experimental and computed spectra of triazenes. Factors such as environment, anharmonicity, Fermi resonance, solvent effects, scale factor for each level of theory, and so forth, are usually not even considered in computations. The experimental value is an anharmonic frequency, while the calculated value is a harmonic frequency [25].

The detailed vibrational analysis of triazenes **1a-1f** is summarized in Table 3. Assignment of all vibrational bands has been carried out on the basis of the DFT calculations. A linearity

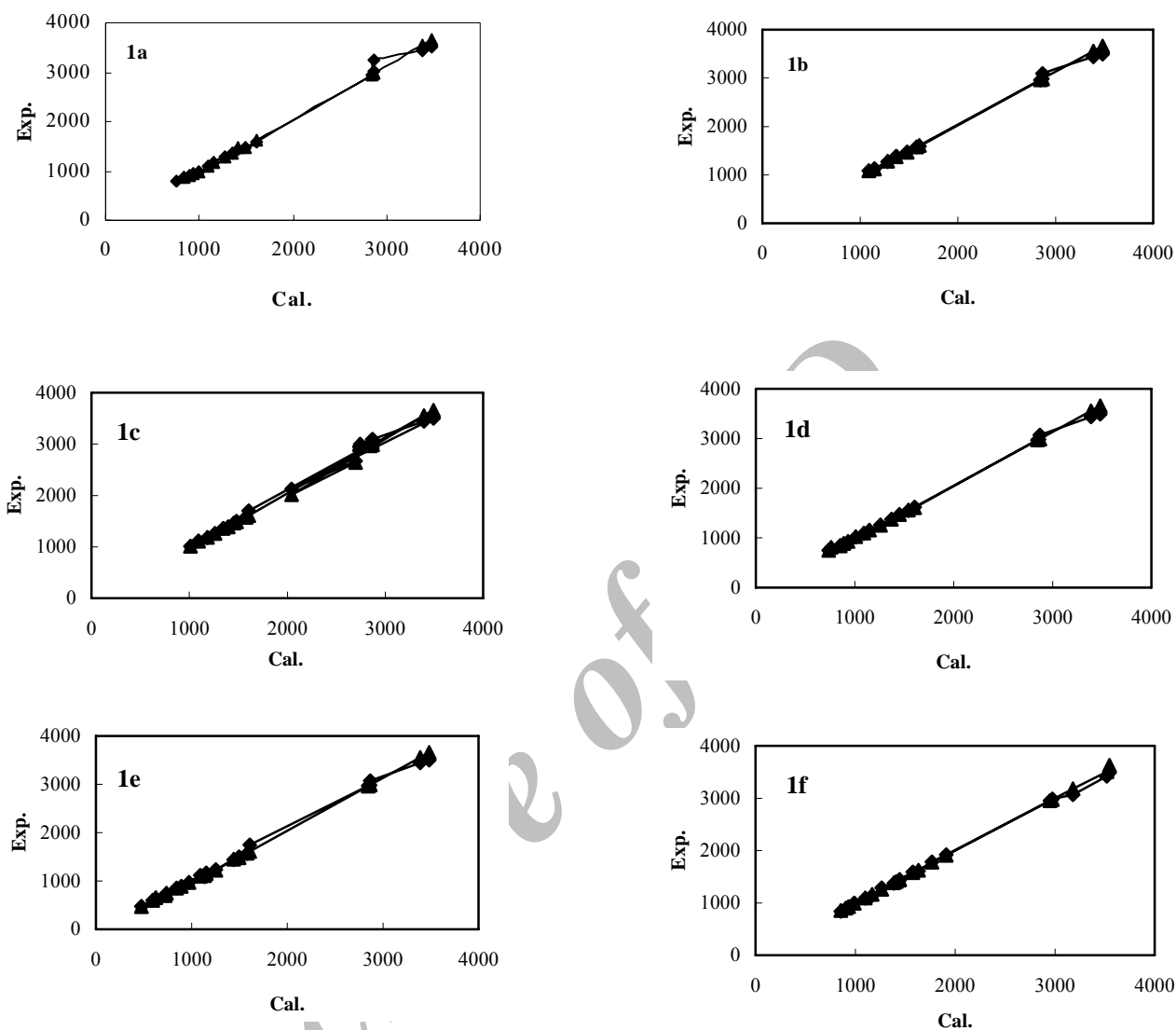


Fig. 3. Correlations between the experimental and theoretical frequencies (cm^{-1}) obtained by the HF (\blacklozenge) and B3LYP/6-31G* (\blacksquare) methods.

between the experimental and calculated wave numbers (i.e. for the whole spectral range considered), can be estimated by plotting the calculated *vs.* experimental wave numbers (Fig. 3). The values of the correlation coefficients, 0.899-0.999, provide good linearity between the calculated and experimental wave numbers. In the case of CH stretching, four modes are expected at 2950-3180 cm^{-1} .

These vibrations are observed at 2940-3075 cm^{-1} in the IR spectra of the triazenes. The bands corresponding to the NH_2 stretching vibrations belong to the SO_2NH_2 and are expected near

3416-3498 cm^{-1} in the IR spectrum of triazenes **1a-1f**. The bands observed at 1450-1680 cm^{-1} are assigned to the ring stretching modes of the aromatic ring. The observed bands at 1245-1370 and 1070-1155 cm^{-1} are assigned to the $\nu(\text{SO}_2)_{\text{asym.}}$ and $\nu(\text{SO}_2)_{\text{sym.}}$ modes, respectively. The C-H out-of-plane bending vibrations are expected in the range of 820-960 cm^{-1} . The calculations also show that the $\pi(\text{CH})$ vibrations are not pure and contain significant contributions of other modes [$\nu(\text{SN})$ and $\pi(\text{CN})$]. The S-N stretching vibration exhibits a moderate band in the region of 900-950 cm^{-1} ; the band observed in this region is

Table 4. Calculated and Observed Visible Absorption Maxima of Triazenes **1a-1f**

Compound	Calculated $\lambda_{cal}(nm)^b$	Ethanol $\lambda_{obs}(nm)^a$	Acetone $\lambda_{obs}(nm)^a$	DCM $\lambda_{obs}(nm)^a$	Acetonitrile $\lambda_{obs}(nm)^a$	DMF $\lambda_{obs}(nm)^a$
1a	364	259	260	260	264	262
1b	371	259	260	260	263	262.5
1c	369	259.5	261	260.5	263.5	263
1d	380	258.5	261	260	263.5	263
1e	370	259	260	260.5	263.5	262.5
1f	366	260	260	261	263.5	263

^aObserved visible absorption. ^bCalculated visible absorption maxima based on the CIS method.

not pure $\nu(SN)$ vibration and contains a significant contribution of the $\pi(CH)$ mode. The bands at 450-550 cm^{-1} are assigned to the SO_2 scissors and SO_2 wagging vibration, and partly overlap in this region. Calculations show that $\omega(SO_2)$ vibration contains a considerable contribution with the π ring [26]. The major bands in the 550 cm^{-1} region relate to a S-C stretch, and in the 970 cm^{-1} region to a CH_2 twist, rock and wag. Minor spectral detail contributions were observed in the 1365 cm^{-1} region for a CH_2 scissors in this spectrum.

UV-Vis Spectra

The λ_{max} of various triazenes were calculated by the configuration interaction singles (CIS) method. The observed and calculated visible λ_{max} of these compounds in this study are given in Table 4. Calculations of molecular orbital geometries show that the visible absorption maxima of these triazenes correspond to the electron transition from HOMO to LUMO. The λ_{max} is a function of the electron availability; so the moieties with stronger donor character push more electrons into the rings, resulting in a larger λ_{max} . The electronic spectra of these dyes showed an absorption band in the region 258.5-360 nm in ethanol, 260-261 nm in acetone, 260-261 nm in dichloromethane (DCM), 263-264 nm in acetonitrile and 262-263 nm in dimethylformamide (DMF). The λ_{max} of the investigated azo dyes show larger bathochromic shifts in DMF than in other solvents. UV-Vis spectra of triazenes **1a-1f** in various solvents are shown in Fig. 4.

CONCLUSIONS

This investigation predicted that the vibrational frequencies and visible spectra of triazenes **1a-1f** could be successfully

elucidated by the HF and B3LYP methods using basis sets. The fittings between calculated and measured vibrational frequencies were achieved by the HF and B3LYP theoretical levels, and the deviations between calculated and experimental values are quite small for a given type of vibration. Therefore, this study confirms that the theoretical calculation of the vibrational frequencies for triazenes is quite useful for determining the vibrational assignment and for predicting new vibrational frequencies.

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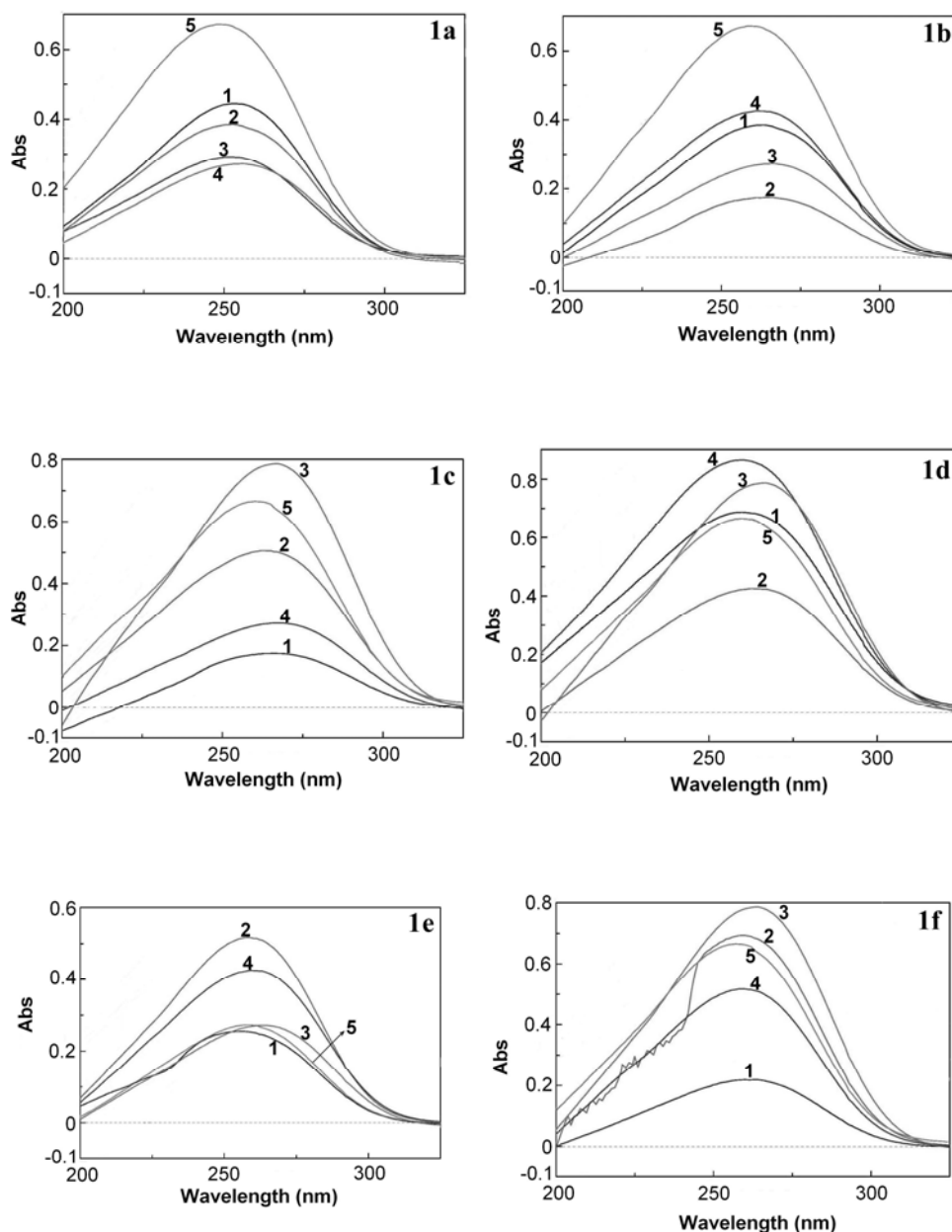


Fig. 4. UV spectra of triazene **1a-1f** in various solvents: (1) CH_2Cl_2 , (2) Acetone, (3) DMF, (4) Acetonitrile, (5) Ethanol.

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