

Effect of Solvent polarities on the molecular properties of 2-(2-nitrovinyl) furan

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ABSTRACT

This study investigated the effects of solvents' polarities on the geometry and electronic properties of 2-(2-nitrovinyl) furan, (NVF). The investigation was carried via theoretical approach, using an ab-initio [Hartree Fock (HF/6-31G*)] and Density Functional Theory (DFT/B3LYP/6-31G*). The properties investigated are optimized structures, energy gaps ($E_{\text{LUMO}} - E_{\text{HOMO}}$) and associated global properties, chemical potential (χ), global hardness (η), ionization energy (IE), Electron affinity (EA), dipole moment (μ), polarizability (α) and electronic charges. NVF was sparingly soluble in water, very soluble and more active in polar organic solvent than non-polar solvents. The solvent polarities do not change the structural parameters of NVF widely, but have significant changes on the electron density re-distribution. The highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the molecule showed π -characters, an indication of intermolecular charge transfer characteristics for the excitation of electrons in NVF. The change in the dipole moment associated with low energy gaps for NVF in the polar solvent showed that NVF has strong activity in the solvents. The theoretical data obtained in this study are in good agreement with the earlier reported experimental data.

Keywords: Mulliken charges; global hardness; geometry; electron affinity, polarizability

1. INTRODUCTION

Furfural and its derivatives are very important industrial chemicals and in the biological sciences as starting materials for the synthesis of myriads of pharmaceuticals and in many industrial processes [1, 2, 3]. This makes the applications of 2-(2-nitrovinyl) furan (NVF) as antibacterial, antifungal and anti-ectoparasitic agent (Figure 1). These applications have attracted the attention of many researchers over the years [4, 5, 6]. NVF has been reported to have high chemical potentials, with greater growth inhibition zone against the tested

microorganisms such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Fusarium solani* and *Candida albicans* than the tested conventional antibiotics [7].

The properties and applications of many compounds originate essentially at the molecular level [8]. It is essential to understand the electronic structures of NVF via the photo-physical properties (such as oscillator strength, dipole moment and polarizability), as well as, the Frontier Molecular Orbital (FMO): HOMO) and LUMO energy levels. The electronic

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properties of molecules have contributed to the generation of exciton and charge transfer characteristics of the molecules [8], of which NVF may be of no exception. A good understanding of the important steps to explain how the studied properties of the molecule occurred and modified will go a long way to improve the quality of this molecule for the development and synthesis of new compounds with improved properties [9].

The frontier molecular orbital (FMO) characteristics and their associated properties [such as electronegativity/chemical potential (χ), global chemical hardness (η), nucleophilicity and electrophilicity index (ω)] play significant roles in the prediction of the stabilities and efficiency of molecules. These properties aid in the understanding of the relationship between the moieties constituting structure, chemical behaviours and performance in gas phase and any other media [10]. Adequate knowledge, in this regard will serve as guide to assist chemists in the development and synthesis of new derivatives of compounds with improved desirable properties [11].

Partial atomic charges, i.e. Mulliken, electrostatic and natural charges have also found useful applications in the molecular modeling. These parameters have been used to explain structural and reactivity differences in various molecules and their conformers [12, 13] in addition to investigation of charge transfers within a single molecule and between several molecules [14]. The effect of solvents on the energies and associated electronic properties of organic compounds are often related to the dielectric constant of the solvent, so long the specific solvent effects such as hydrogen bonding and donor acceptor interactions are not present [14].

The Density functional theory (DFT) and Hartree-Fock (HF) are very popular cost

effective general procedures for investigating the physical properties and charge distribution over all atoms in many body organic systems. Although, DFT has been reported to have, refined, better model the exchange and correlation interactions in molecules. It generates data that are in good agreement with experimental data [9, 15, 16]. It partitions electronic energy into electronic kinetic energy, electron nuclear attraction and electron-electron repulsion terms [16]. The hybrid functional, Becker's three-parameter exchange functional and nonlocal correlation functional of Lee-Yang-Parr modification (B3LYP) has also been stated to be highly successful for calculating the electronic properties [17, 18].

This study investigated the sensitivity of electronic properties of NVF in solvents having different polarities. Two different quantum mechanical methods (HF/6-31G* and DFT/B3LYP/6-31G*) were employed to determine the Mulliken charges, dipole moment, polarizability, frontier molecular orbital parameters and associated activity properties of the studied compound.

The principle of hard-soft-acid-base (HSAB) was employed to examine various chemical situations quantitatively to describe the interaction energy between solvent and NVF molecule, as proposed by Gazquez and Mendez in 1994 and pursued by Pal and co-workers in 2000. DFT has been reported to have refined, and better model the exchange and correlation interactions in molecules. Literature survey reveals that, to the best of our knowledge, no ab-initio; HF or DFT calculations of NVF have been reported before now.

2. METHODOLOGY

2.1 Computational details

Using the molecular editor builder of Spartan' 14 software package, NVF ($C_6H_5NO_3$), was modelled. Its energy was minimized (Figure 1) and subjected to

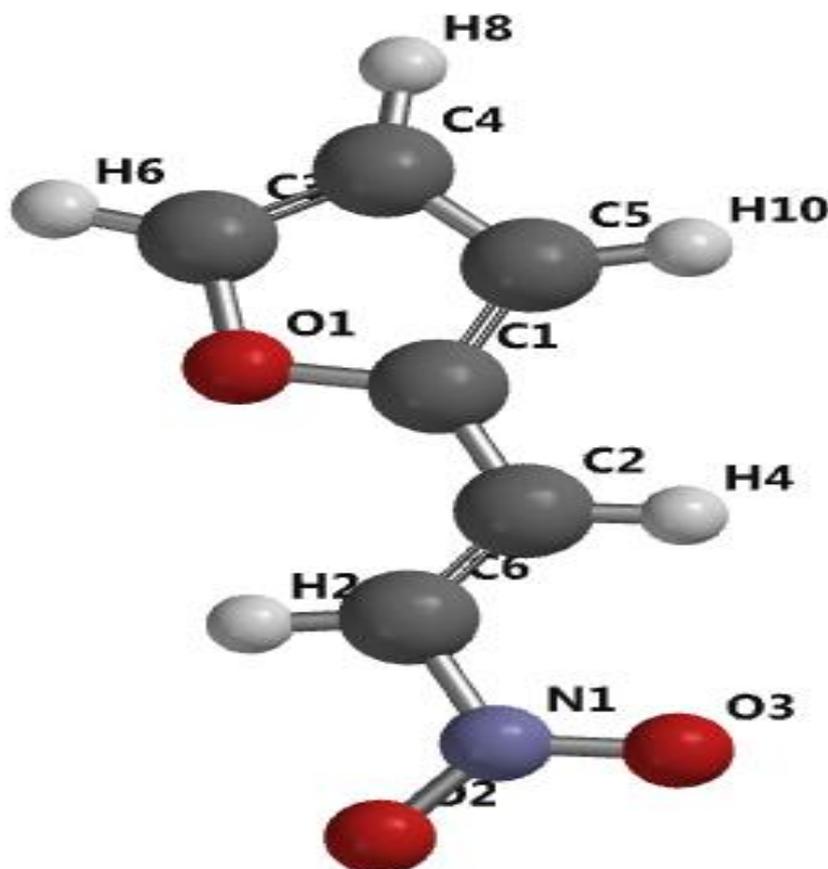
optimization of geometry, using equilibrium geometry at ground state with molecular orbital calculation at HF/6-21G* and DFT/B3LYP/6-21G* levels of theories in vacuum and solvent of different polarity function index at SM8 model [19]. The calculated ground state molecular geometry parameters: μ , α , Mulliken charges, the frontier molecular orbital (HOMO and LUMO) energies, $E_{\text{LUMO}} - E_{\text{HOMO}}$, interaction energy and electrostatic potential minimums and maximums of the studied molecules were from energy calculations at the same levels of theories (HF/6-21G* and DFT/B3LYP/6-21G*). The associated frontier molecular orbital energy properties, such as: IE global softness (S) and global hardness (η), global electrophilicity index (ω) and nucleophilicity index were also determined [20, 21].

Table 1. Solvent polarity index

Solvent	Polarity index			
	n	ϵ	μ (D)	ΔP
DCM	1.424	9.08	1.14	0.219
Ethanol	1.361	25.30	1.69	0.290
Water	1.338	80.5	1.85	0.318
DMSO	1.479	47.2	3.96	0.263
Toluene	1.497	2.38	0.31	0.0136

Solvent polarity function
 $\Delta P = \left(\frac{\epsilon-1}{2\epsilon+1} - \frac{n^2-1}{2n^2+1} \right)$, ϵ , n and μ are solvent the dielectric constant, refractive index and dipole moment respectively (Adeoye, 2018).
 (DCM = dichloromethane, DMSO = dimethylsulphoxide)

3. RESULTS

**Fig. 1.** Optimized structure of 2- (2-nitrovinyl) furan.

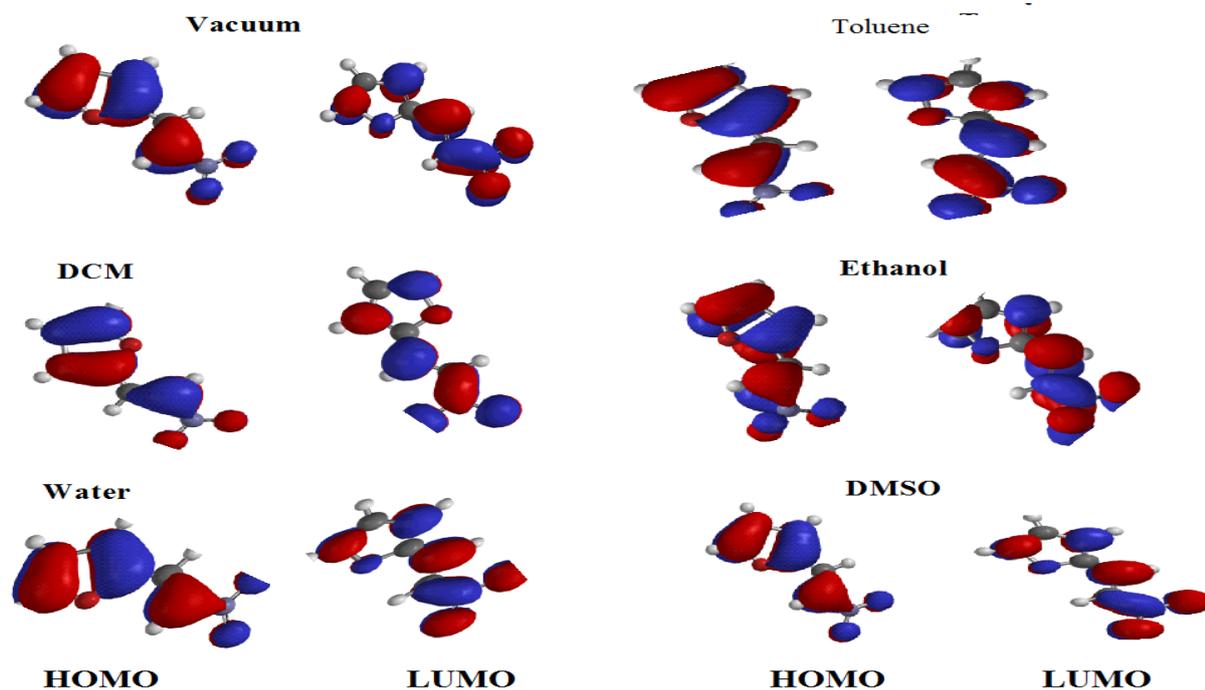


Fig. 2. Electronic densities /HOMO and LUMO energies diagram of 2-(2-nitrovinyl) furan in different solvent at the DFT/6-31G* level of theory.

Table 2. DFT obtained FMO and related Quantum Chemical Parameters Energies of NVF in the solvent of different polarities

Molecular Properties	SOLVENT					
	Vacuum	Toluene	DCM	Ethanol	DMSO	H ₂ O
E_L (eV)	-2.62	-2.54	-2.55	-2.75	-3.3	- 2.83
E_H (eV)	-6.51	-6.33	-6.19	-6.26	5.55	- 6.28
Energy gap	3.89	3.79	3.64	3.51	2.25	3.45
Chemical potential (k)	-1.95	-1.90	-1.82	-1.76	-1.13	-1.72
Hardness (η)	1.95	1.90	1.82	1.76	1.13	1.72
Softness (S)	0.26	0.26	0.28	0.28	0.44	0.29
Electrophilicity (ω)	0.99	0.95	0.94	0.88	0.56	0.85
Electronegativity	4.57	4.44	4.37	4.51	4.43	4.56
Ionization energy (I) (eV)	6.51	6.33	6.19	6.26	5.55	6.28
Electron affinity (EA) (eV)	2.62	2.54	2.55	2.75	3.30	2.83
Polarizability, α (\AA^3)	51.15	51.19	51.22	51.26	51.54	51.28
Dipole moment, μ (D)	6.44	7.60	8.69	9.82	9.38	10.34
Total Energy(a.u)	-511.9354	-511.9434	-511.9464	-511.9465	-511.8499	-511.9441
E_{solv} (KJ/mol)	-17.33	NA	NA	NA	NA	NA
Minimum Electrostatic potential (KJ/mol)	-181.45	-200.81	-221.29	-244.25	-220.31	-254.40
Maximum Electrostatic potential (KJ/mol)	156.95	173.57	189.83	202.31	199.3	223.89

E_s = Solvation energy (a. u), I= ionization potential, EA= Electron affinity, E_H = HOMO energy, E_L = LUMO energy and η =global hardness, NA= Not available

Table 3. HF obtained FMO and the related Quantum Chemical Parameters Energies of NVF in the solvent of different polarities

Properties	SOLVENT					
	Vacuum	Toluene	DCM	Ethanol	DMSO	H ₂ O
E _H (eV)	-8.90	-8.66	-8.52	-8.56	-8.46	-8.57
E _L (eV)	1.30	1.36	1.36	1.18	1.38	1.10
Energy gap (eV)	10.2	10.02	9.88	9.74	9.84	9.67
Chemical potential (χ) (eV)	-5.10	-5.01	-4.94	-4.87	-4.92	-4.83
Hardness (η) (eV)	5.1	5.01	4.94	4.87	4.92	4.83
Softness (S) (eV)	0.098	0.099	0.101	0.102	0.101	0.103
Electrophilicity (eV)	2.55	2.51	2.47	2.44	2.46	2.42
Electronegativity	3.8	3.65	3.58	3.69	3.54	3.74
Ionization energy (I) (eV)	8.92	8.66	8.52	8.56	8.46	8.57
Electron affinity (EA) (eV)	-1.30	-1.36	-1.36	-1.18	-1.38	-1.10
Polarizability, α (Å ³)	49.56	49.60	49.64	49.68	49.65	49.69
Dipole moment, μ (D)	6.42	7.11	7.68	8.2	7.85	8.43
Total Energy (a.u)	-508.9893	-508.9993	-509.0016	-508.9997	-508.9997	-508.9962
E _{solv} (KJ/mol)	-8.87	NA	NA	NA	NA	-8.87
Minimum Electrostatic potential (KJ/mol)	-188.24	-201.59	-213.07	-224.24	-215.40	-228.81
Maximum Electrostatic potential (KJ/mol)	165.77	179.57	190.37	196	192.33	198.50

E_s = Solvation energy (a. u), I= ionization potential, EA= Electron affinity, E_H = HOMO energy, E_L = LUMO energy and η =global hardness, NA= Not available

Table 4. Milliken charges analysis of NVF in the vacuum and solvent of different polarities

ELEMENT	Vacuum		Water		DMSO		Toluene		DCM		Ethanol	
	DFT/6-31G*	HF/6-31G*										
C1	+0.350	+0.355	+0.363	+0.323	+0.654	+0.325	+0.349	+0.341	+0.352	+0.329	+0.360	+0.325
C2	-0.157	-0.181	+0.227	-0.152	+0.076	-0.162	-0.169	-0.170	-0.173	-0.162	-0.176	-0.154
C3	+0.105	+0.138	+0.087	+0.134	-0.050	+0.125	+0.091	+0.131	+0.081	-0.162	+0.086	+0.133
C4	-0.178	-0.291	-0.173	-0.325	-0.234	-0.327	-0.188	-0.312	-0.188	-0.325	-0.178	-0.326
C5	-0.190	-0.243	-0.160	-0.211	-0.051	-0.225	-0.185	-0.239	-0.180	-0.230	-0.167	-0.217
C6	+0.006	-0.068	+0.022	-0.083	-1.200	-0.088	+0.002	+0.262	+0.004	-0.084	+0.017	-0.083
H2	+0.193	+0.273	+0.210	+0.288	+0.218	+0.275	+0.195	+0.277	+0.280	+0.253	+0.208	+0.287
H4	+0.209	+0.281	+0.227	+0.315	+0.259	+0.308	+0.212	+0.295	+0.220	+0.306	+0.225	+0.313
H6	+0.177	+0.237	+0.231	+0.286	+0.238	+0.284	+0.202	+0.262	+0.223	+0.280	+0.228	+0.284
H8	+0.160	+0.230	+0.201	+0.257	+0.240	+0.259	+0.181	+0.245	+0.195	+0.253	+0.198	+0.255
H10	+0.161	+0.238	+0.216	+0.286	+0.234	+0.289	+0.190	+0.262	+0.208	+0.279	+0.212	+0.283
N1	+0.431	+0.560	+0.420	+0.583	-0.224	+0.566	+0.429	+0.564	+0.422	+0.567	+0.420	+0.577
O1	-0.449	-0.580	-0.459	-0.605	-0.301	-0.597	-0.446	+0.564	-0.449	-0.590	-0.455	-0.598
O2	-0.413	-0.462	-0.511	-0.554	-0.214	-0.517	-0.433	-0.490	-0.454	-0.514	-0.484	-0.542
O3	-0.402	-0.487	-0.497	-0.542	-0.113	-0.516	-0.430	-0.504	-0.459	-0.517	-0.495	-0.535

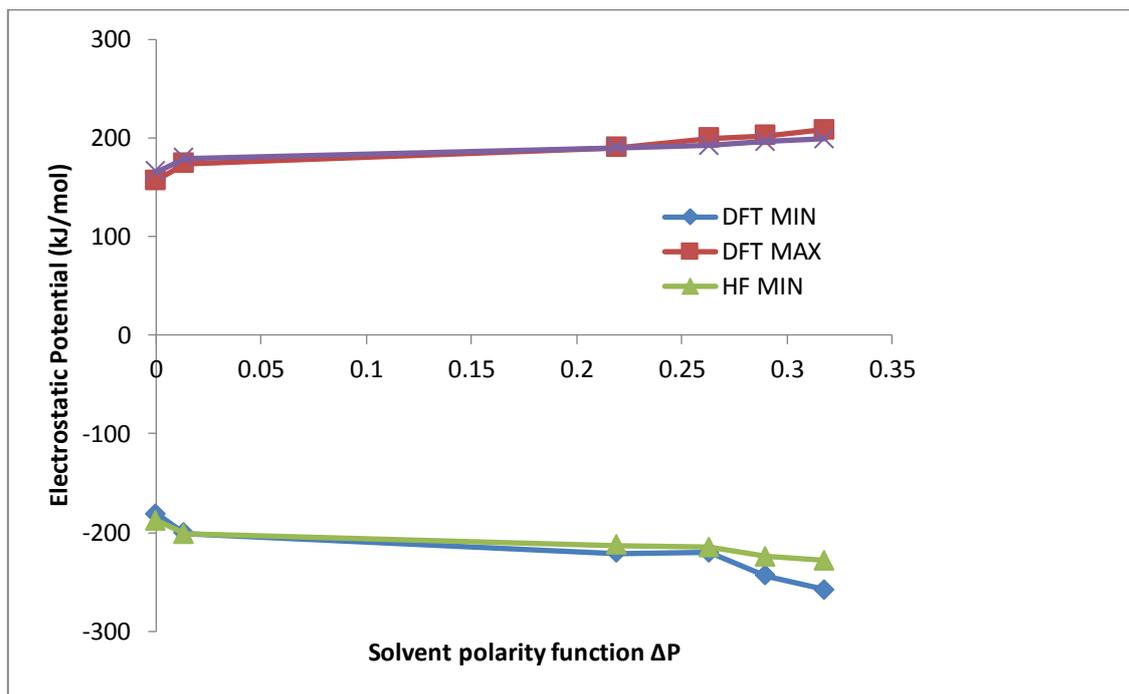


Fig 3. Relationship between solvent polarity function ΔP and electrostatic potential (KJ/mol) of the molecule in different solvent.

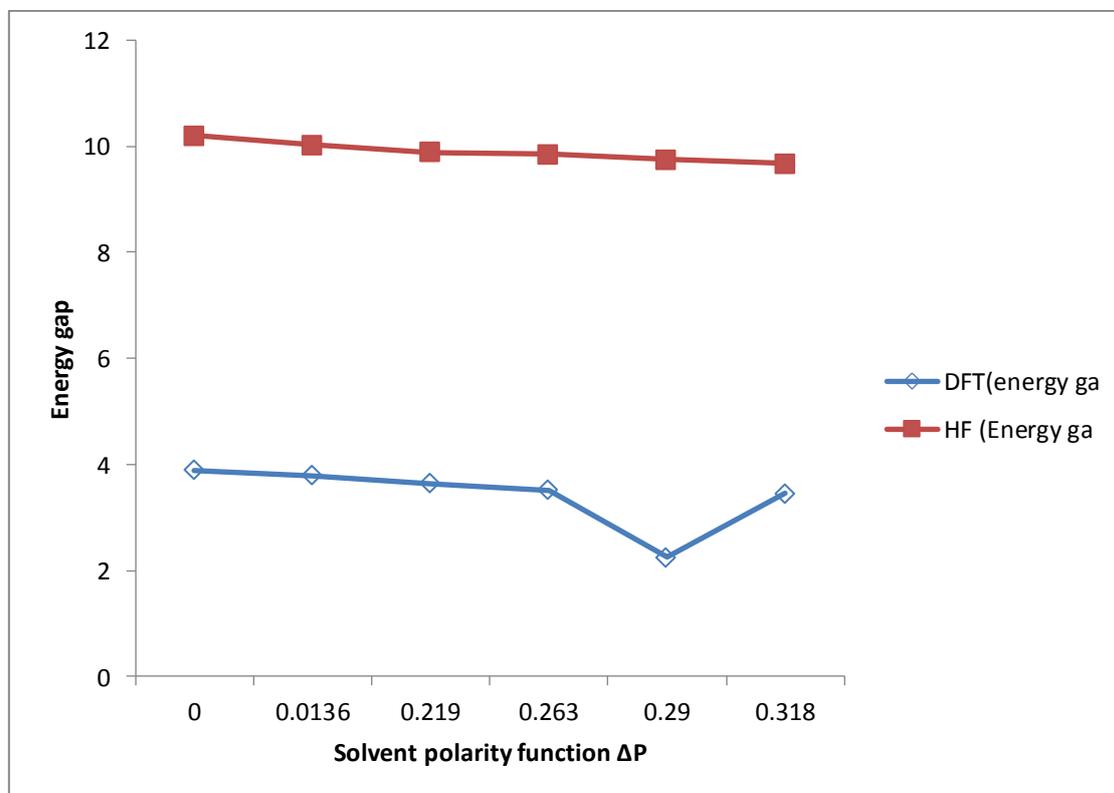


Fig. 4. Relationship between the Energy gap of NVF in different solvent and solvent polarity function.

Table 5. Electrostatic charges analysis of NVF in the vacuum and solvent of different polarities

ELEMENT	Vacuum		Water		DMSO		Toluene		DCM		Ethanol	
	DFT/ 6-31G*	HF/ 6-31G*										
C1	+0.395	+0.386	+0.395	+0.351	+0.453	+0.368	+0.370	+0.375	+0.364	+0.365	+0.347	+0.353
C2	-0.070	-0.098	-0.070	-0.068	-0.066	-0.081	-0.063	-0.087	-0.048	-0.081	-0.020	-0.070
C3	-0.131	-0.148	-0.131	-0.163	-0.090	-0.159	-0.135	-0.160	-0.138	-0.164	-0.124	-0.168
C4	-0.328	-0.345	-0.328	-0.307	-0.342	-0.326	-0.306	-0.333	-0.297	-0.325	-0.263	-0.310
C5	+0.184	+0.206	+0.184	+0.220	+0.195	+0.219	+0.190	+0.212	+0.195	+0.217	+0.188	+0.218
C6	+0.161	+0.173	+0.161	+0.181	+0.168	+0.181	+0.167	+0.179	+0.172	+0.181	+0.167	+0.182
H2	+0.191	+0.212	+0.191	+0.222	+0.207	+0.225	+0.200	+0.217	+0.206	+0.221	+0.197	+0.221
H4	-0.177	-0.199	-0.177	-0.216	-0.189	-0.212	-0.169	-0.202	-0.173	-0.205	-0.167	-0.211
H6	-0.269	-0.212	-0.269	-0.137	-0.293	-0.171	-0.232	-0.190	-0.213	-0.170	-0.188	-0.145
H8	+0.202	+0.204	+0.202	+0.208	+0.212	+0.209	+0.187	+0.207	+0.187	+0.208	+0.175	+0.208
H10	-0.232	-0.317	-0.232	-0.382	-0.259	-0.360	-0.259	-0.339	-0.276	-0.360	-0.262	-0.377
N1	+0.169	+0.199	+0.169	+0.215	+0.165	+0.206	+0.173	+0.203	+0.177	+0.207	+0.173	+0.213
O1	+0.774	+0.956	+0.774	+0.969	+0.842	+0.962	+0.781	+0.960	+0.784	+0.965	+0.723	+0.968
O2	-0.431	-0.506	-0.437	-0.551	-0.491	-0.534	-0.448	-0.520	-0.463	-0.533	-0.468	-0.546
O3	-0.437	-0.511	-0.431	-0.539	-0.512	-0.527	-0.457	-0.520	-0.477	-0.528	-0.486	-0.536

Table 6. Natural charges analysis of NVF in the vacuum and solvent of different polarities

ELEMENT	Vacuum		Water		DMSO		Toluene		DCM		Ethanol	
	DFT/ 6-31G*	HF/ 6-31G*										
C1	+0.255	+0.265	+0.255	+0.248	+0.230	+0.254	+0.246	+0.265	+0.241	+0.257	+0.244	+0.251
C2	+0.142	+0.203	+0.142	+0.219	+0.141	+0.210	+0.147	+0.203	+0.156	+0.209	+0.162	+0.216
C3	-0.333	-0.353	-0.333	-0.361	-0.324	-0.360	-0.335	-0.353	-0.335	-0.359	-0.319	-0.361
C4	-0.255	-0.243	-0.255	-0.219	-0.231	-0.230	-0.249	-0.243	-0.239	-0.234	-0.223	-0.224
C5	+0.235	+0.231	+0.235	+0.261	+0.256	+0.239	+0.243	+0.231	+0.251	+0.237	+0.253	+0.239
C6	+0.256	+0.253	+0.256	+0.257	+0.278	+0.257	+0.264	+0.253	+0.269	+0.256	+0.272	+0.257
H2	+0.253	+0.254	+0.253	+0.261	+0.272	+0.262	+0.265	+0.254	+0.271	+0.259	+0.272	+0.261
H4	-0.450	-0.539	-0.450	-0.548	-0.439	-0.544	-0.451	-0.539	-0.452	-0.540	-0.435	-0.545
H6	-0.226	-0.140	-0.226	-0.105	-0.209	-0.122	-0.206	-0.140	-0.193	-0.125	-0.198	-0.110
H8	+0.284	+0.275	+0.284	+0.283	+0.292	+0.280	0.282	+0.275	+0.284	+0.279	+0.284	+0.282
H10	-0.107	-0.147	-0.107	-0.173	-0.120	-0.164	-0.119	-0.147	-0.128	-0.161	-0.108	-0.170
N1	+0.260	+0.260	+0.260	+0.267	+0.262	+0.260	+0.261	+0.260	+0.263	+0.262	+0.265	+0.266
O1	+0.484	+0.644	+0.484	+0.646	+0.432	+0.644	+0.481	+0.644	+0.477	+0.645	+0.419	+0.646
O2	-0.411	-0.470	-0.387	-0.502	-0.426	-0.485	-0.424	-0.470	-0.440	-0.483	-0.449	-0.496
O3	-0.387	-0.495	-0.411	-0.514	-0.414	-0.502	-0.406	-0.495	-0.426	-0.502	-0.440	-0.510

Table 7. Bond order and Electron density analysis of NVF in different solvent

Element	Mulliken Bond order											
	Vacuum		Water		DMSO		Toluene		DCM		Ethanol	
	DFT/ 6-31G*	HF/ 6-31G*	DFT/ 6-31G*	HF/ 6-31G*	DFT/ 6-31G*	HF/ 6-31G*	DFT/ 6-31G*	HF/ 6-31G*	DFT/ 6-31G	HF/ 6-31G*	DFT/ 6-31G*	HF/ 6-31G*
C1 C3	0.094	0.067	0.077	0.064	0.205	0.065	0.085	0.078	0.082	0.066	0.079	0.065
C1 C5	1.477	1.654	1.457	1.636	1.555	1.643	1.489	1.419	1.476	1.643	1.463	1.638
C1 H6	-	-	-	-	0.028	-	-	-	-	-	-	-
C1 O1	0.973	0.935	0.949	0.918	0.934	0.923	0.975	0.953	0.966	0.928	0.955	0.922
C1 C2	1.175	1.091	1.214	1.110	1.060	1.106	1.184	1.229	1.196	1.103	1.208	1.107
C1 H4	-	-	-	-	-0.121	-	-	-	-	-	-	-
C1 C6	0.031	-	0.028	-	-0.797	-	0.028	0.036	0.029	-	0.028	-
C1 H2	-	-	-	-	-0.100	-	-	-	-	-	-	-
C1 O3	-	-	-	-	0.031	-	-	-	-	-	-	-
C3 C4	1.582	1.725	1.556	1.717	1.443	1.721	1.585	1.517	1.572	1.719	1.560	1.717
C3 C5	-	-	-	-	0.065	-0.025	-	-	-	-0.025	-	-0.025
C3 H6	0.927	0.926	0.905	0.899	0.923	0.900	0.917	0.908	0.908	0.902	0.906	0.900
C3 O1	1.063	0.988	1.097	0.986	0.795	0.987	1.075	1.109	1.087	0.991	1.093	0.989
-	-	-	-	-	-	-	-	-	-	-	-	-
C3 C2	-	-	-	-	0.032	-	-	0.037	0.028	-	0.032	-
C3 C6	0.046	-	0.039	-	0.075	-	0.042	0.043	0.042	-	0.040	-
C4 C5	1.320	1.244	1.327	1.253	1.230	1.253	1.311	1.335	1.321	1.255	1.326	1.254

Continues Table 7												
C4 H6	-	-	-	-	-0.047	-	-	-	-	-	-	-
C4 H8	0.929	0.922	0.914	0.909	0.861	0.908	0.921	0.916	0.916	0.911	0.915	0.910
C4 H10	-	-	-	-	-0.054	-	-	-	-	-	-	-
C4 O1	0.069	0.045	0.053	0.040	0.037	0.042	0.064	0.058	0.058	0.042	0.054	0.041
C4 C6	-	-	-	-	-0.223	-	-	-	-	-	-	-
C5 H10	0.928	0.917	0.905	0.891	0.882	0.889	0.916	0.910	0.909	0.895	0.907	0.893
C5 C2	-	-	-	-	0.027	-	-	-	-	-	-	-
C5 H4	-	-	-	-	-0.051	-	-	-	-	-	-	-
C5 O1	0.046	0.028	0.055	-	-	0.026	0.049	0.062	0.052	0.027	0.054	0.026
C5 C6	0.080	0.056	0.067	0.055	-0.186	0.056	0.074	0.071	0.071	0.056	0.068	0.055
O1 C2	-	-	-	-	-0.089	-	-	-	-	-	-	-
O1 C6	-	-	-	-	0.117	-	-	-	-	-	-	-
C2 H4	0.899	0.896	0.898	0.882	0.801	0.885	0.897	0.899	0.897	0.886	0.898	0.883
C2 C6	1.650	1.809	1.520	1.728	1.608	1.756	1.620	1.485	1.582	1.761	1.539	1.737
C2 H2	-	-	-	-	-0.117	-	-	-	-	-	-	-
C2 N1	-	-	0.043	-	-0.080	-	-	0.042	0.030	-	0.039	-
C2 O2	0.056	0.031	0.050	0.032	0.131	0.032	0.054	0.05	0.054	0.032	0.055	0.032
C2 O3	0.048	0.034	0.055	0.033	0.285	0.034	0.050	0.055	0.050	0.034	0.051	0.033
C6 H4	-	-	-	-	0.245	-	-	-	-	-	-	-
C6 H2	0.914	0.907	0.900	0.896	1.156	0.905	0.912	0.901	0.908	0.902	0.902	0.897
C6 N1	0.886	0.854	1.019	0.906	0.809	0.884	0.924	1.023	0.957	0.882	1.001	0.899
	-	-	-	-	-	-	-	0.046	-	-	-	-
C6 O2	-	-	0.061	-	-0.091	-	-	0.074	0.028	-	0.032	-
C6 O3	0.049	-	0.035	-	-0.325	-	0.053	-	0.055	-	0.059	-
N1 H2	-	-	-	-	-0.041	-	-	1.376	-	-	-	1.401
N1 O2	1.460	1.483	1.340	1.388	1.804	1.426	1.444	1.329	1.427	1.430	1.401	1.444
N1 O3	1.434	1.487	1.389	1.437	2.046	1.463	0.409	0.250	1.386	1.462	1.354	0.160
O2 O3	0.266	0.176	0.222	0.158	0.293	0.165	0.254	-	0.242	0.165	0.228	-

Table 8. DFT calculated bond angle (°) and bond length (Å) analysis of NVF in different solvent

Atoms	Bond Length (Å)					
	Vacuum	Toluene	DCM	Water	DMSO	Ethanol
O2N1	1.238	1.239	1.242	1.258	1.244	1.247
N1O3	1.237	1.240	1.244	1.250	1.246	1.25
C6N1	1.444	1.436	1.43	1.417	1.427	1.421
C2C6	1.337	1.348	1.351	1.357	1.352	1.355
C1C2	1.420	1.425	1.422	1.415	1.420	1.417
C1O1	1.378	1.376	1.377	1.392	1.387	1.386
C3O1	1.355	1.356	1.356	1.366	1.363	1.361
C3C4	1.371	1.366	1.368	1.368	1.366	1.368
C5C4	1.415	1.421	1.419	1.416	1.418	1.417
C1C5	1.390	1.378	1.380	1.381	1.379	1.381
C1C3	2.217	2.195	2.195	2.206	2.203	2.201
Bond angles (°)						
O3N1C6	115.81	116.27	116.54	117.05	116.81	116.85
O2N1C6	118.96	119.65	119.95	120.52	120.02	120.31
O1C1C2	123.89	119.27	119.36	119.72	119.51	119.4
O1C1C5	107.37	109.25	109.23	109.12	109.22	109.12
O2N1O3	125.22	124.08	123.51	122.43	123.39	122.84
C3O1C1	108.46	106.93	106.88	106.27	106.41	106.5
C2C6N1	119.63	120.61	120.80	120.94	120.85	120.90
C1C2C6	119.73	125.39	125.19	125.00	125.47	125.04
C4C5C1	107.95	106.93	106.87	107.22	107.08	107.08
C5C4C3	105.82	105.84	105.95	106.25	106.09	106.08
C2C1C5	128.74	131.48	131.41	131.16	131.27	131.46

4. DISCUSSION

4.1 Electron Distributions in 2-(2-nitrovinyl) furan and associated properties

4.1.1 Molecular geometry

Figure 1 presents the planar geometry of the optimized structure of 2-(2-nitrovinyl) furan (with minimization energy of -20.802 kJ/mol. The interaction of any system at the molecular level depends on both electron donating and accepting character of the system, which in turn is a function of the substituent(s) on such system [22]. The plane of furan (C₃-O₁-C₁) remains unchanged in terms of torsion angles around (C₃-O₁-C₁-C₂) and (C₃-O₁-C₁-C₅) in the studied solvents, indicating the decrease in the potential energy stored within the molecule, with NVF being more stable in the observed conformation

However, the changes in the distribution of charges for the NVF as a result of the difference in the local environment/solvent have effect on its bond lengths and bond angles (Table 7). This is because solvent polarity determines the intermolecular forces of the molecule via the electrostatic interaction between them. These affect the physical properties of the compound. Both methods show good agreement in the observed values of bond angles and bond lengths for the atoms in NVF. Although, in general, the HF/ 6-21G* results are slightly lesser than those of DFT/B3LYP/6-21G*, except in few cases.

The calculated geometry parameters have been affirmed to represent a good approximation which can be the basis for calculating other parameters despite the differences. These include molecular electrostatic potential, dipole moment and polarizability. It was observed that the bond lengths of C₁O₁, C₃O₁, C₆ N₁, N₁O₃ and N₁O₂ are different from their

corresponding SP³ hybridized bond length [11]. The bond lengths increase with increasing solvent polarity and highest in water. The C₁O₁ and C₃O₁ bond lengths are also higher than those of N₁O₃ and N₁O₂. This may be due to loss of conjugation of n-electrons of O₁ atom to C₁ and C₃. This causes the concomitant lesser distribution of π-electron, as a result of strong tendency of intermolecular hydrogen bonding of the molecule in protic polar solvent. This may probable cause the observed changes in the bond angles with change in solvent polarity.

3.1.2 Mulliken charges and other molecular properties

As earlier posited, the important characteristics of a molecule is the distribution of its electron density. Calculation of the electron density distribution enables one to predict the dipole moment, polarizability, the charge distribution, the bond orders, and the shapes of various molecular orbitals of a system [11]. Also, in the application of quantum mechanical calculations to molecular system, the calculation of effective atomic charges plays an important role [23]. Tables 3-6 present the Mulliken, natural, electrostatic potential (ESP) charges and related properties for the studied molecules while Figures 2-4 show the variation of these parameters with solvent polarity (measured by ΔP).

The electrostatic potential (ESP) predicts the site of protonation on a molecule by rationalising the intermolecular interaction between two polar species and defined the region of local negative and positive potentials on it. It assists in predicting the path in which the charges will take as they approach the molecule [24]. The two quantum mechanical methods show good agreement

in their minimum and maximum electrostatic potential obtained, however, the two ESP values vary in reverse direction. The minimum ESP decreases with increasing solvent polarity, while the maximum ESP exhibits the opposite (Figure 3). The large tendency of charge transfer characteristic of NVF from oxygen moiety of the furan ring to the oxygen atoms of the nitro group, serve to increase the volume over which the charges are distributed. These result into its lower electrostatic energy which vary in different solvent (Figure 3, Table 3).

The partial charges on NVF can further be explained by ESP map (Supplementary Figure 2) which arises from the differences in the electronegativity of the bonding atoms in NVF

The map describes the electrostatic potentials at the surfaces of NVF, which are represented by different colors. The negative (red and yellow) and the positive (blue) regions in the map were related to the electrophilic and nucleophilic reactivity respectively. As can be visualized from it, the negative region of the title structure is localized more on the oxygen atom (red coloured portions) of the nitro group, an indication of the region of minimum electrostatic force (excess electron), and acting as electrophilic attack. The positive region (deep blue and light blue regions) are observed around the O1 C2,C4, H6 and H8 atoms, an indication of the region of maximum of electrostatic force (nucleophilic reactivity region). From the map, it was also observed that the red and yellow regions are greater in polar solvent, most especially in water and DMSO. These signify that the compound may have intermolecular interactions (activity) with the solvent more at .this regions.

The partial charges on NVF can further be explained by electrostatic potential map (Supplementary Figure 2) which arises from the differences in the

electronegativity of the bonding atoms in NVF. The charge distribution as visualized from the map, indicate the minimum electrostatic force (excess electron) on the nitro group oxygen (red coloured portions, acting as electrophilic attack, while the blue region indicate the maximum of electrostatic potential [24, 25].

The Mulliken charges (a measure of the electron population) on each atom of NVF vary significantly with solvent polarities, while the electrostatic and natural charges slightly vary in the two levels of theories (Tables 4-6). Bond orders have been used to explain whether a species is free or covalently bonded. It has also been proposed as an index of progress along a reaction coordinate, since bond is a manifestation of the electron density between two nuclei.

The calculated bond orders (Table 7) are quite sensitive to solvent polarities and the level of theories used for its calculation. The result shows that there are high population of charges on the polar bonds (C₁C₅, C₁C₂, C₃C₄, C₂C₆, N₁O₂ and N₁O₃), and this is highest in C₂C₆. The result portrays diffused function describing the charge population on the atoms that are not directly linked (i.e. adjacent) to each other. This observation indicates that solvent polarities have significant effect on the orbital interactions within this molecule.

There are also observed changes in partial charges on the atoms of NVF in the studied solvent. Increasing solvent polarity is accompanied with decrease in charges carried by the negatively charged atoms O₁, O₂, O₃ and C₂. C₄ C₅ atoms, with attendant increase in the charges carried by positively charged atoms (C₃, C₅, and C₆). These attests to the charge transfer characteristics tendency inherent in NVF molecule.

3.1.2 Molecular orbital energies and related parameters

The DFT and HF calculated FMO (E_{HOMO} and E_{LUMO}) which are useful parameters for determining the stability/activities of molecules, as well as, their mode of interaction with the solvent themselves or any other molecules are as presented in Table 2. FMO describes where electrons reside within a molecule, as well as, the probability of finding electron(s) at a particular point in its space. The energy of the HOMO is directly related to the ionization potential while that of the LUMO is related to the electron affinity [26]. The high value of HOMO in any molecule is an indication of its high tendency to donate electron to molecules with empty and low lying energy orbital acting as an acceptor. Large HOMO–LUMO energy gap is an indication of high stability and consequently less activity for the molecule in chemical reactions [27].

The molecular orbitals in NVF have extension over all the atoms in the molecule (Figures 2-5). The polarity of solvent do not change the structural parameters of NVF widely, but due to redistribution of atomic charges in this molecule in different solvent, there are significant changes in the magnitudes of studied global properties. Both the HOMO and the LUMO show π -characters. The π -characters are more delocalize over the furan ring and the C=C double bond in conjugation with the furan ring in the HOMO. Whereas the LUMO are delocalized over the entire molecule, most importantly on the nitro group. This is an indication of intra-molecular charge transfer characteristics for excitation of electron within the molecule. The analysis of the wave function of NVF indicates that electron densities are transfer to NO_2 moiety through the C=C bond in conjugation with the furan ring. These observations are peculiar to this molecule

in all solvent of choice for both DFT and HF calculated results.

From Table 2, the total energy (in a. u) of NVF in the solvents is relatively small and inversely depends on solvent polarity. The values obtained were found to be smallest in water and highest in DMSO. The energy difference in the gas phase and the solvent media was significant for both methods. DFT results have lower energy than that of HF. Similar trends were also observed for the computed $E_{\text{LUMO}} - E_{\text{HOMO}}$ for the compound in solvent media. The $E_{\text{LUMO}} - E_{\text{HOMO}}$ decrease with increasing solvent polarities, and followed the trend: $\text{DMSO} < \text{H}_2\text{O} < \text{CH}_3\text{CH}_2\text{OH} < \text{DCM} < \text{Toluene} < \text{Vacuum}$ in DFT, while in the HF theory, the trend: $\text{H}_2\text{O} < \text{CH}_3\text{CH}_2\text{OH} < \text{DMSO} < \text{DCM} < \text{Toluene} < \text{Vacuum}$ were observed. These indicate that the solubility and conductivities of NVF increases with increasing solvent polarities (Table 1). The small $E_{\text{LUMO}} - E_{\text{HOMO}}$ values are characteristic of easily excited molecules because only minimal energy needs to be overcome during electron transitions [28]. This data suggests NVF to be most stable or less reactive comparatively in toluene and least in vacuum, indicating that solvent has high influence on its activity. This is in agreement with the overall energy of the molecule (Table 2 and 3). The DFT result also corroborated the earlier reported experimental results, that the compound was sparingly soluble in water and highly soluble in polar organic solvent [4]. The differences observed in the data obtained from both methods may be due to the different assumptions and simplifications in attainment of their theories. For instance, Hartree–Fock calculations are sometimes said to ignore, or at least neglect the electron correlation in its own applications [16, 29].

3.2 Electronic properties

The electronic properties obtained for the studied molecules in solvent of different polarities, from the two quanta mechanical methods are electronegativity χ , IP, EA, ω , global hardness (η) and absolute softness (S) are as presented in Tables 2 and 3. The electronegativity value as estimated by Mulliken, indicated by: $\frac{(I + EA)}{2}$ is a measure of inductive effect of an atom or group of atoms in a molecule [30]. For reaction between two atoms of different electronegativities, the electrons flow from the molecule with the lower electronegativity towards that of higher electronegativity until the chemical potentials are at equilibrium [31]. The higher the electronegativity values of a molecules, the higher is its activity.

The DFT/B3LYP/6-31G* and HF/6-31G* computed electronegativity values for NVF is lower in non-protonated organic solvent than the protonated one, but highest in vacuum. It lower values in protonated solvent may be due to the hydrogen bonding tendency of NVF with these solvent.

IE ($-E_{\text{HOMO}}$) is a measure of stability and chemical inertness of a compound is of the order: DMSO < Vacuum and DCM < Ethanol < H₂O < Toluene, indicating its easy ionization in DMSO, and hence, its highest activities and solubility in it (Figure 2). The electron acceptor ability of a molecule, measured by its Electron Affinity (EA) is expressed through LUMO orbital energies as: $-E_{\text{LUMO}}$. Molecules with higher HOMO energy are more reactive with electron loving species, while those with lower LUMO energy are essential for molecular reactions involving nucleus loving species. The EA values for NVF in different solvents of choices are of the order: DMSO > H₂O > CH₃CH₂OH > Vacuum > DCM > Toluene which is also attesting to its highest activities and solubility in DMSO. This trend also

supported the earlier reported findings of Alabi and Hassan in 2014, which affirmed that the NVF was sparingly soluble in water, highly soluble in polar organic solvent and insoluble in non-polar solvents.

The η and S which are important molecular properties for measuring the resistance of a molecule to charge transfer and solvation ability followed the trends: Vacuum > Toluene > DCM > CH₃CH₂OH > water > DMSO and DMSO > H₂O > CH₃CH₂OH > DCM > Vacuum > Toluene for DFT/B3LYP/6-31G* computed results respectively. But, for HF/P/6-31G* computed results, the trends; Vacuum > Toluene > DCM > DMSO > CH₃CH₂OH > water and H₂O > CH₃CH₂OH > DMSO > DCM > Vacuum > Toluene were followed (Figures 3 and 4). These parameters, using Koopmans' theorem [31] within a HF and/or DFT schemes as expressed by Mulliken (1934) signifies the easiness/resistance towards the dissociation/polarization of the electron cloud of the atoms, ions or molecules in chemical reaction [33]. Since hard molecules have large energy gaps, low solvation and low ability to transfer charges and vice versa [33, 34], NVF has highest and lowest activities in DMSO and toluene respectively for the DFT/B3LYP/6-31G* computed results, while in the HF/6-31G* computed results, NVF was highest in water. The DFT/B3LYP/6-31G* results supports Alabi and Hassan, 2014 claims.

Electrophilicity index (ω) concept measures the tendency of chemical species to accept electrons and the resistance of the system to exchange electronic charge with the environment, expressed in terms of two global activity indices, chemical potential (\bar{k}) and chemical hardness (η) as: $\omega = \bar{k}^2 / \eta$, decreases with increasing solvent polarities for both DFT/B3LYP/6-31G* and HF/6-31G* computed results. The

higher values of HF /6-31G* result reflects the high correlation energy of this method. Thus, the DFT and HF calculated variables from, using 6-31G* basis set revealed that the electrons capturing tendency of the NVF increases with increasing solvent polarity.

The dipole moment and polarizability of any molecule represent a measure of bond properties, charge densities in a molecule and their activities [35]. Molecules with better charge distribution and increasing distance have higher dipole moment and Polarizability [36]. Both the dipole moment and polarizability (Tables 2 and 3) obtained from the levels of theories follows the trend: Vacuum < Toluene < DCM < DMSO < Ethanol < water, indicating an increase in the average polarizability and dipole moment for the compound as solvent polarities increase. This supports the experimental findings that NVF is soluble and more reactive in polar solvent [4]. But, the electron correlation inherent in DFT model probably tends to lower the values of these parameters, to bring it closer to the experimental value [16].

4. CONCLUSION

The total energies of the NVF, from DFT/B3LYP/6-31G* and HF/6-31G* computed results, slightly decrease (more negative), as solvent polarities increase. This indicate that the solvent interaction with NVF is *exothermic* (thermodynamically favorable). The energy gap of the studied molecule decreases with increasing solvent polarities, indicating small excitation energies of manifold of the exited states. The DFT/B3LYP/6-31G* and HF/6-31G* computed results provide supports for the earlier experimental results for the conductivities, solubility and activities of NVF in non-polar and polar solvent. It

also confirmed that the compound has highest chemical activity in the polar DMSO.

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