Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Real-time Spectroelectrochemical Monitoring of the Diazonium Electrografting

Supporting Information

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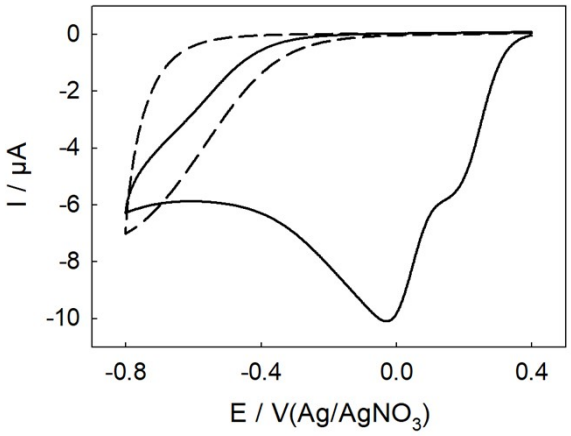


Figure S1. First (—) and second (---) CV cycles recorded on a GC electrode at 50 mV/s in CH_3CN, 0.1 M nBu_4NPF_6 containing 1 mM of 4-nitrobenzenediazonium under atmospheric conditions.

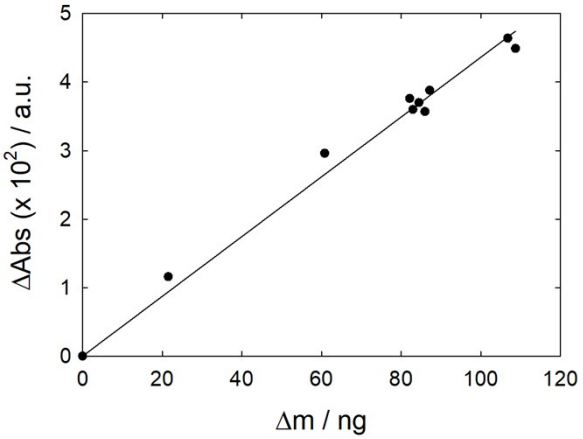


Figure S2. Correlation between Δabs and Δm respectively recorded on GC electrode and carbon-coated quartz crystal during two cyclic voltammograms between +0.4 and -0.8 V in the presence of 1 mM of 4-NBD.

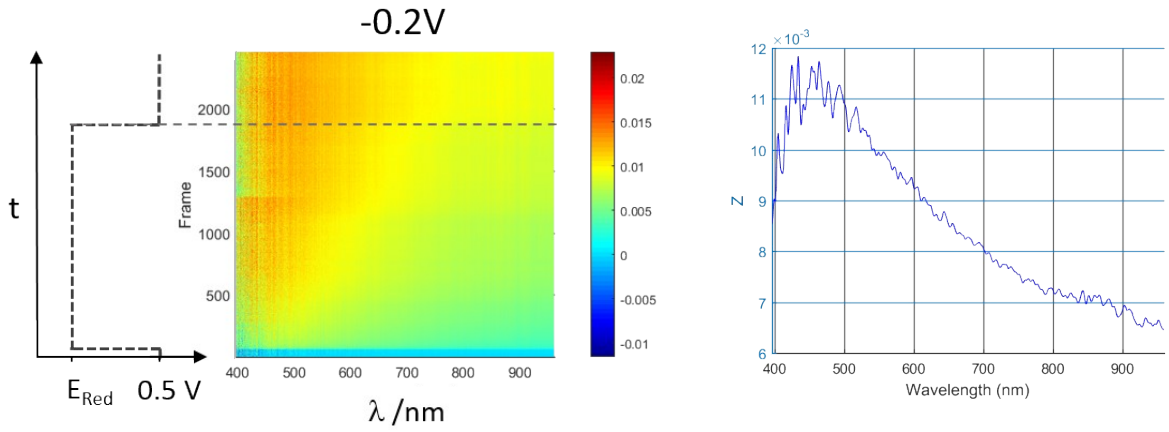


Figure S3. A-SEC of chronoamperometric experiments recorded on glassy carbon in the presence of 1 mM 4-NBD in atmospheric conditions for E_{Red} = -0.2 V. Potential program: 30 s at +0.5 V, 15 min at E_{Red}, 5 min at +0.5 V (left). Absorption spectrum extracted for E_{Red} = 8 min (frame n°1020) from the A-SEC (right).

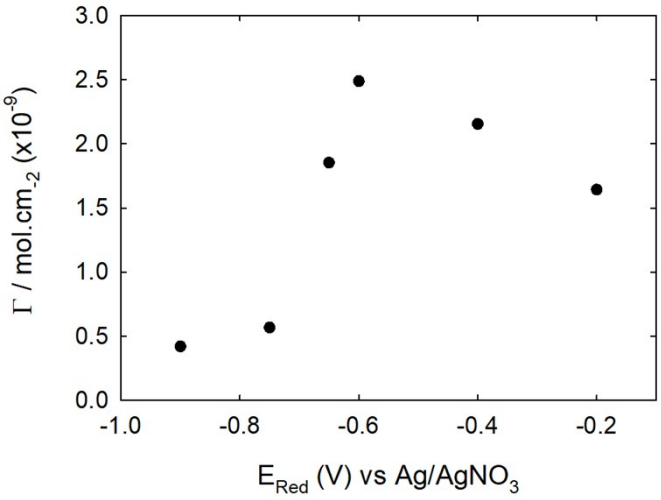


Figure S4. Nitrophenyl surface coverage on a modified carbon electrode as a function of the potential applied. Potential program: 30 s at +0.5 V, 15 min at E_{Red}, 5 min at +0.5 V.

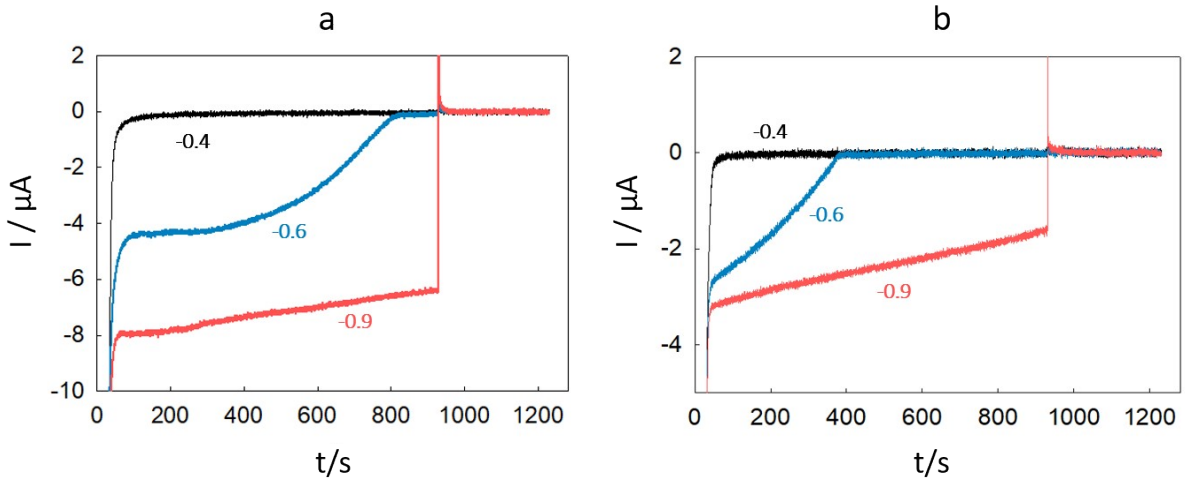


Figure S5. Current-time curves recorded during the A-SEC experiments on glassy carbon (a) and polycrystalline gold (b) in the presence of 1 mM 4-NBD under atmospheric conditions for E_{Red} = -0.4, -0.6 and -0.9 V. Potential program: 30 s at +0.5 V, 15 min at E_{Red}, 5 min at +0.5 V.

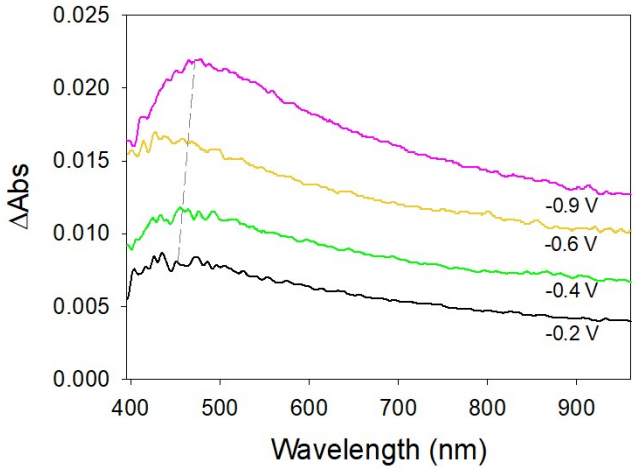


Figure S6. Absorption spectrum extracted for E_{Red} = 8 min from the A-SEC measurement recorded on glassy carbon in the presence of 1 mM 4-NBD under inert atmosphere. Potential program: 30 s at +0.5 V, 15 min at E_{Red}.

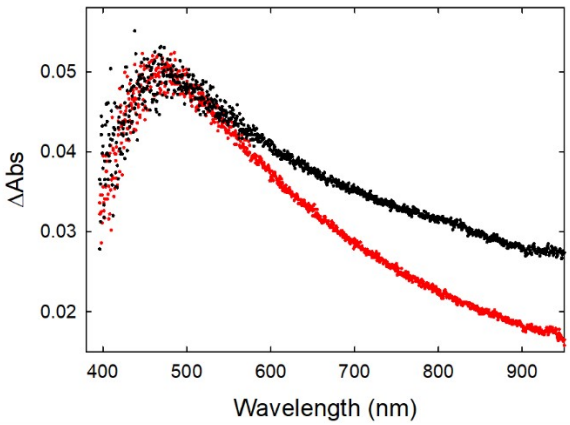


Figure S7. Absorption spectrum extracted for E_{Red} = 15 min from the A-SEC measurement recorded on glassy carbon in the presence of 1 mM 4-NBD under inert atmosphere (black) and atmospheric conditions (red). Potential program: 30 s at +0.5 V, 15 min at E_{Red}.

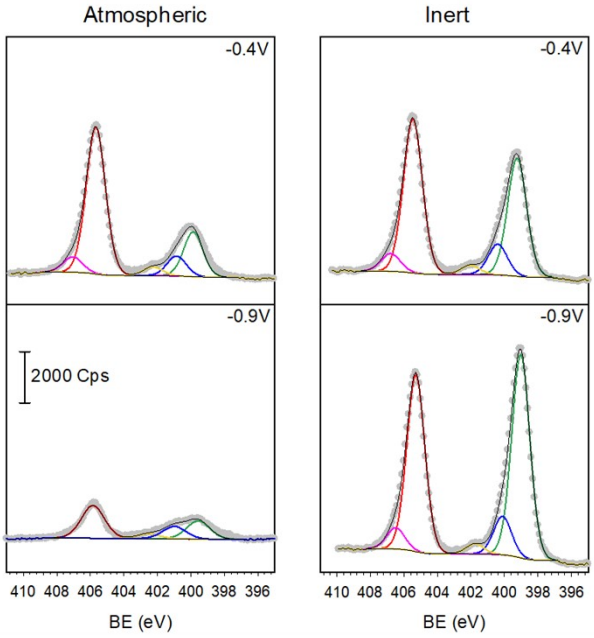


Figure S8. N1s core level spectra for glassy carbon surfaces modified under chronoamperometric condition in the presence of 1 mM 4-NBD under atmospheric (left) or inert (right) conditions at -0.4 and -0.9 V for 15 min.

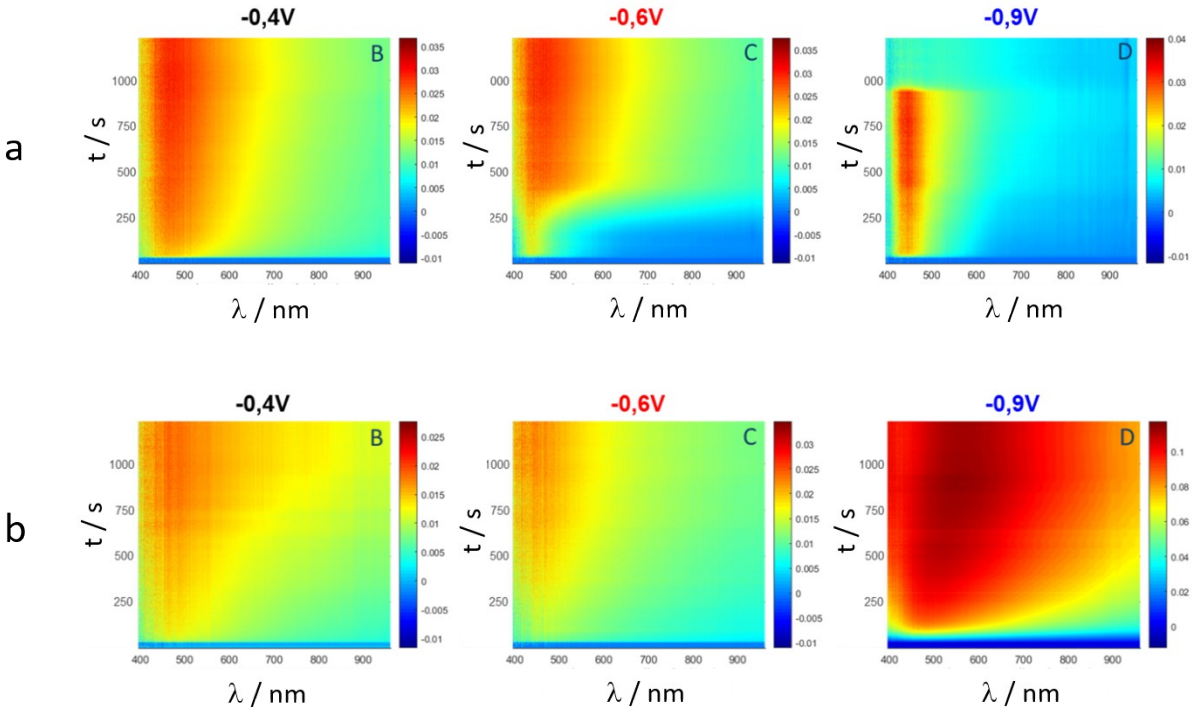


Figure S9. A-SEC of chronoamperometric experiments recorded on glassy carbon in the presence of 1 mM of 1-AQD in atmospheric conditions (**a**) and inert conditions (**b**). Potential program: 30 s at +0.5 V, 15 min at E_{Red} (-0.4 , -0.6 or -0.9 V), 5 min at +0.5 V.

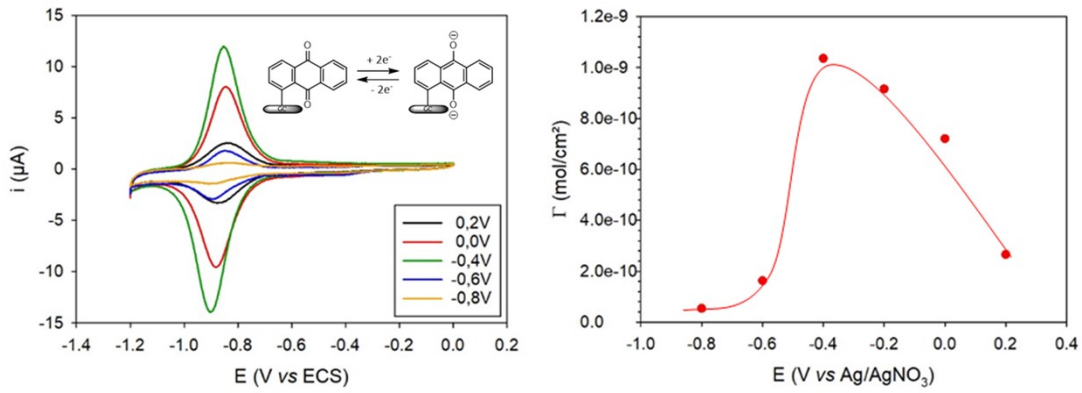


Figure S10. Cyclic voltammograms recorded in KOH 0.1 M on modified glassy carbon electrodes (0.07 cm^{-2}) in the presence of 1 mM AQD at E_{red} for 2 min (left). Anthraquinone surface concentration extracted from the corresponding cyclic voltammograms considering a 2-electron transfer.

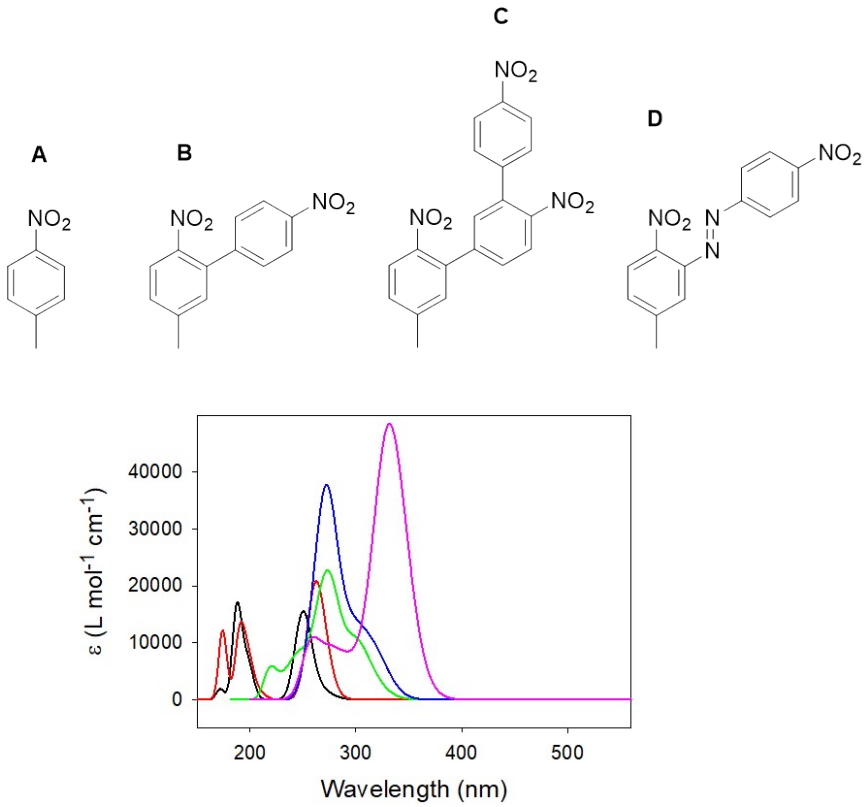
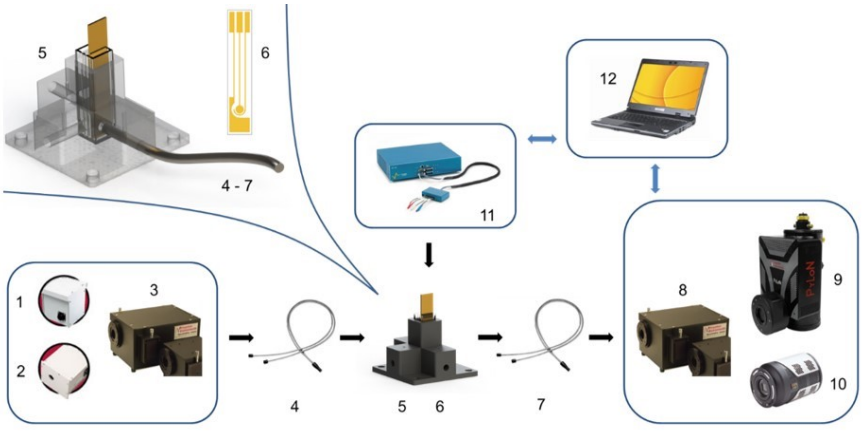


Figure S11. Possible polymeric structures for the film formation from the reduction of nitrobenzene diazonium salt (A ---), B (---), C (---) and D (---).



1 UV source (Tungsten lamp)
2 Visible-NIR source (Halogen lamp)
3 Spectrometer (ACTON SP2155)
4 Fiber optics
5 Analysis cell
6 Modified electrode
7 Fiber optics
8 Spectrometer (ACTON SP2360i)
9 NIR detector (PyLoN-IR-1024-1.7)
10 Visible detector (PIXIS-100B-eXcelon)
11 Potentiostat (Biologic SP150)
12 Control and signal processing

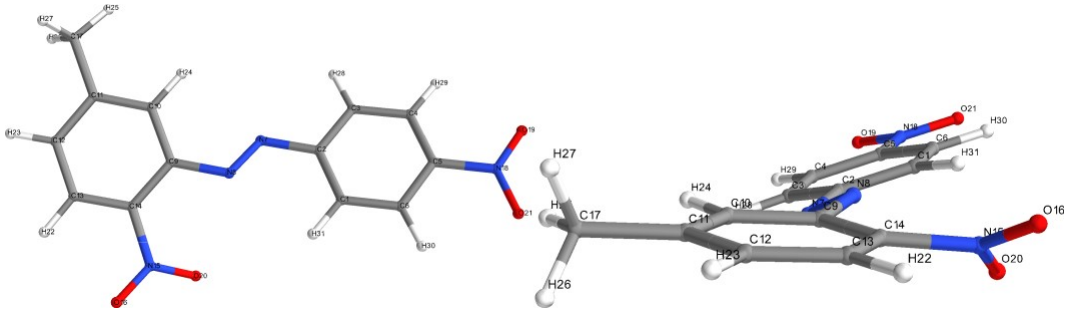
Figure S12. Setup of the Absorption Spectroelectrochemical (A-SEC) bench.

Table S1. UV-Vis calculation report generated by Quchemreport

- **COMPUTATIONAL DETAILS**

Software	Gaussian	(2009+D.01)
Computational method	DFT	
Functional	PBE1PBE	
Basis set name	6-311+G(2d,2p)	
Number of basis set functions	873	
Closed shell calculation	True	
Requested SCF convergence on RMS and Max density matrix	1e-08	1e-06
Requested SCF convergence on energy	1e-06	
Job type: Geometry optimization		
Max Force value and threshold	0.000005	0.000450
RMS Force value and threshold	0.000001	0.000300
Max Displacement value and threshold	0.001348	0.001800
RMS Displacement value and threshold	0.000278	0.001200
Job type: Time-dependent calculation		
Number of calculated excited states and spin state	15	['Singlet-A']
Job type: Frequency and thermochemical analysis		
Temperature	298.15 K	
Anharmonic effects	None	

- **MOLECULE**



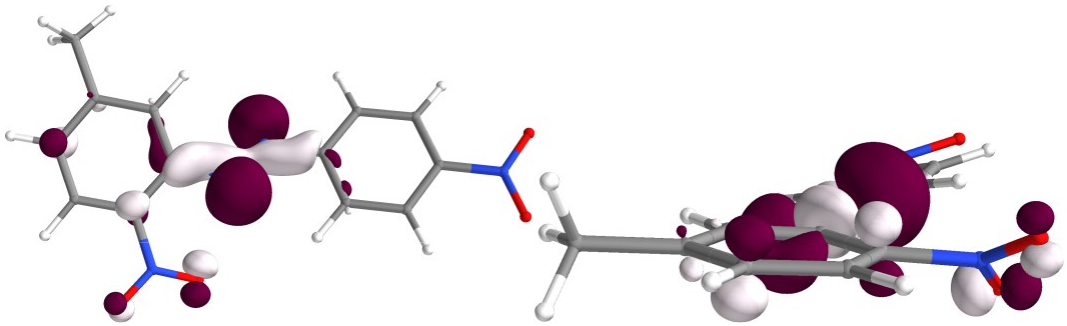
Formula	C13H10N4O4
Charge	0
Spin multiplicity	1

- **RESULTS**

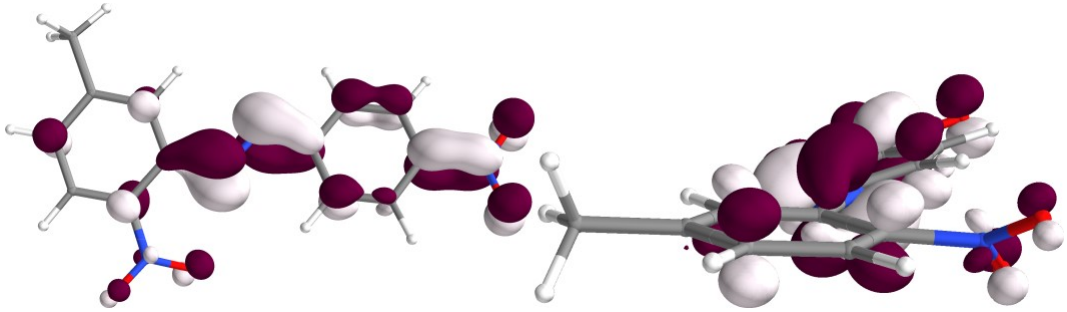
Total molecular energy	-1020.23806 hartrees
HOMO number	74
LUMO+1 energies	-2.52 eV
LUMO energies	-3.39 eV
HOMO energies	-7.41 eV
HOMO-1 energies	-7.77 eV

Geometry optimization specific results

Converged nuclear repulsion energy	1521.57774 Hartrees
Frequency and Thermochemistry specific results	
Enthalpy at 298.15 K	-1019.99520 Hartrees
Gibbs free energy at 298.15 K	-1020.06368 Hartrees
Entropy at 298.15 K	0.00023 Hartrees



Representation of the HOMO from two points of view.

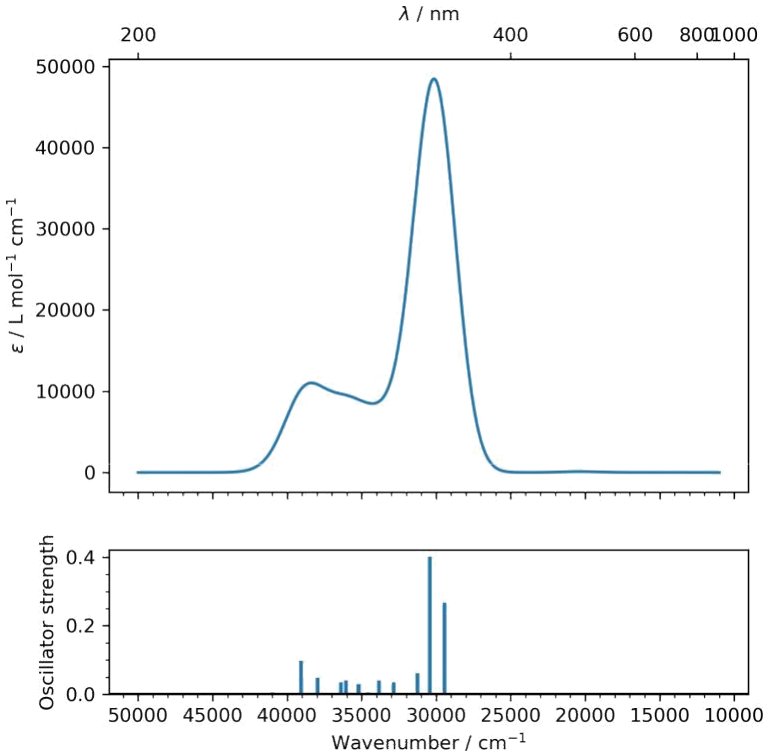


Representation of the LUMO from two points of view.

Results concerning the calculated mono-electronic excitations.

E.S.	Symmetry	nm	cm^{-1}	*f*	R	Λ	d*CT*	q*CT*	Excitation description : initial OM - ending OM (% if > 5%)
1	Singlet-A	493	20260	0.002	30.8	0.54	322.80	0.61	74-75(84);
2	Singlet-A	339	29434	0.268	-18.0	0.53	211.07	0.47	68-76(7); 73-75(36); 74-76(29);
3	Singlet-A	328	30411	0.401	-103.2	0.56	153.72	0.48	73-75(51); 74-76(32);
4	Singlet-A	324	30789	0.0005	6	0.58	316.16	0.59	69-75(39); 69-76(6); 69-77(13); 70-75(24); 70-77(8);
5	Singlet-A	320	31245	0.061	21.3	0.43	475.90	0.66	72-75(73); 74-76(12);
6	Singlet-A	304	32863	0.035	5.4	0.49	208.92	0.72	71-75(93);

7	Singlet-A	295	33843	0.04016.2	0.44	264.45	0.48	68-75(7); 68-76(19); 72-75(9); 72-76(20); 73-76(12); 74-76(11);	
8	Singlet-A	289	34562	0.006	-3.6	0.36	376.04	0.59	67-75(41); 67-76(7); 67-77(12); 74-77(23);
9	Singlet-A	284	35204	0.029	17.7	0.40	65.54	0.53	67-75(22); 67-77(6); 74-77(38);
10	Singlet-A	277	36049	0.040	19.2	0.47	223.75	0.56	73-76(64);
11	Singlet-A 274 36395 0.035 -71.4 0.47 153.75 0.42 66-75(11); 66-76(14); 69-75(8); 70-75(13); 73-76(12); 74-77(15);								
12	Singlet-A 263 37970 0.04881.2 0.49 138.39 0.46 64-76(6); 66-75(6); 66-76(13); 69-75(20); 70-75(30);								
13	Singlet-A	256	39054	0.098	17.5	0.40	451.97	0.61	68-75(60); 72-76(25);
14	Singlet-A	251	39694	0.003	0.1	0.52	267.18	0.48	68-75(9); 73-77(67);
15	Singlet-A 244 40968 0.0055.3 0.33 164.97 0.52 64-75(11); 68-76(6); 71-76(39); 71-77(8); 72-76(9);								

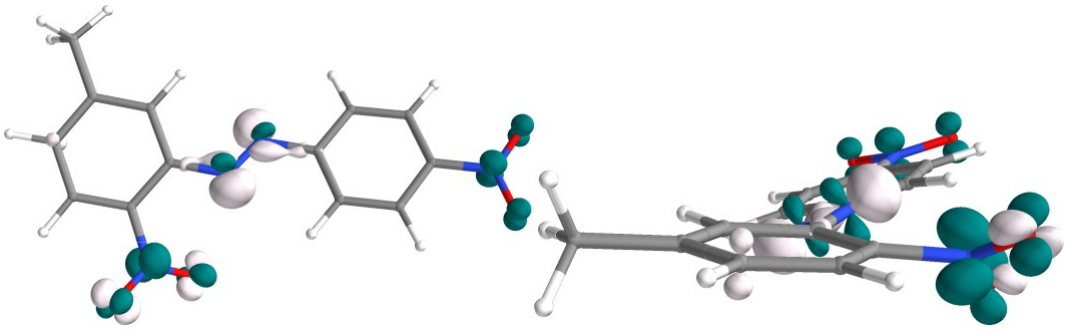


Calculated UV visible Absorption spectrum with a gaussian broadening (FWHM = 3000 cm-1)

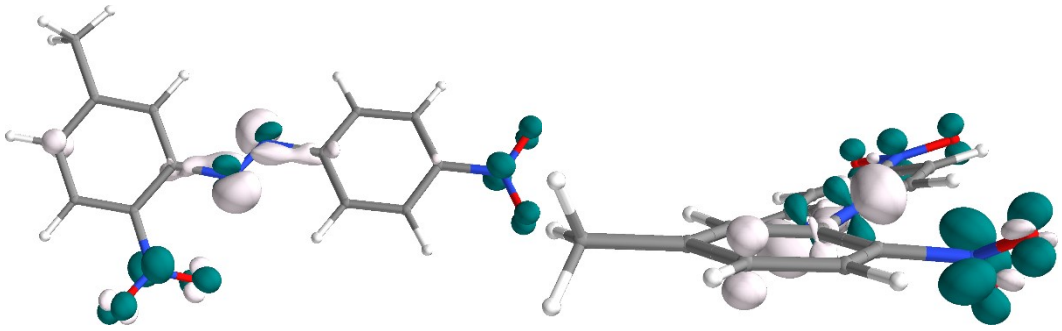
Converged cartesian atomic coordinates in Angstroms

Atom	X	Y	Z
C	-1.8641	0.7596	0.1885
C	-1.3515	-0.4834	-0.1879
C	-2.2035	-1.5470	-0.4719
C	-3.5722	-1.3901	-0.3510

C	-4.0612	-0.1540	0.0344
C	-3.2294	0.9256	0.2990
N	0.0300	-0.7477	-0.3441
N	0.7708	0.1214	0.1435
C	2.1473	-0.1578	0.0358
C	2.6390	-1.4571	0.1334
C	4.0010	-1.7217	0.1588
C	4.8892	-0.6453	0.1019
C	4.4261	0.6540	0.0211
C	3.0641	0.8929	-0.0216
N	2.6178	2.2728	-0.1734
O	3.3190	3.1381	0.3169
C	4.5124	-3.1263	0.2629
N	-5.5118	0.0239	0.1575
O	-6.2168	-0.9362	-0.0845
O	1.5902	2.4688	-0.7916
O	-5.9157	1.1188	0.4952
H	5.1036	1.4952	-0.0222
H	5.9567	-0.8282	0.1244
H	1.9188	-2.2613	0.2115
H	3.6997	-3.8503	0.2290
H	5.2025	-3.3508	-0.5527
H	5.0580	-3.2729	1.1977
H	-1.7743	-2.4904	-0.7825
H	-4.2610	-2.1969	-0.5541
H	-3.6650	1.8730	0.5818
H	-1.1828	1.5783	0.3748

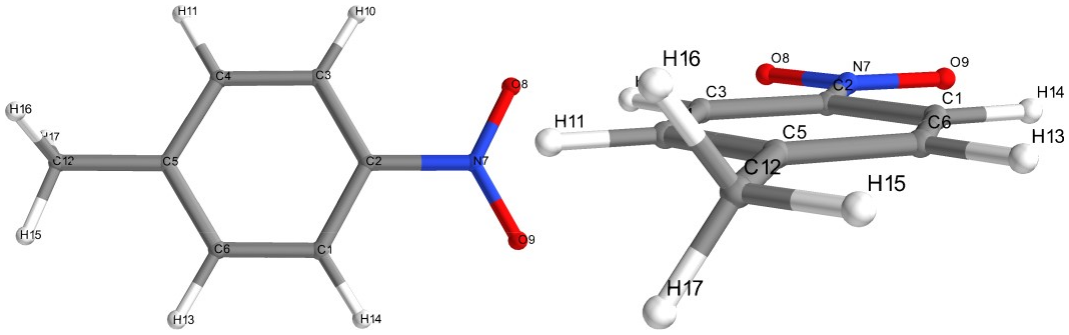


Representation of the Electron Density Difference (S2-S0) from two points of view.



Representation of the Electron Density Difference (S3-S0) from two points of view.

- **MOLECULE**



Chemical structure diagram with atomic numbering from two points of view.

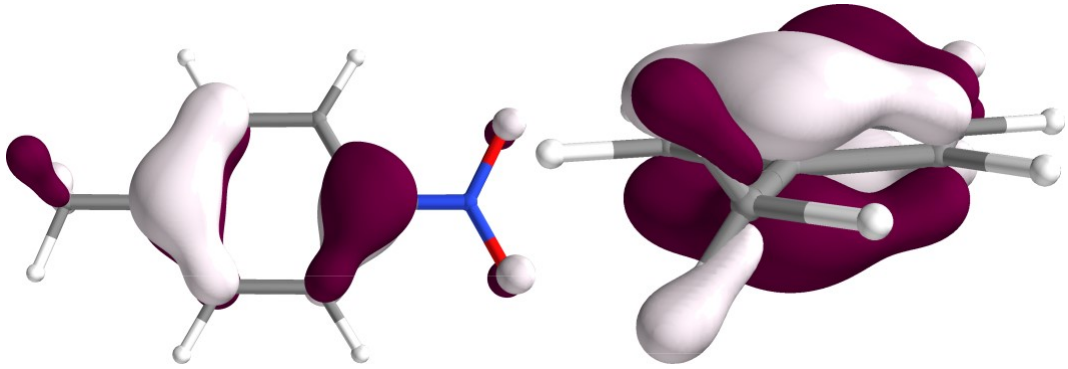
Formula	C7H7NO2
Charge	0
Spin multiplicity	1

- **RESULTS**

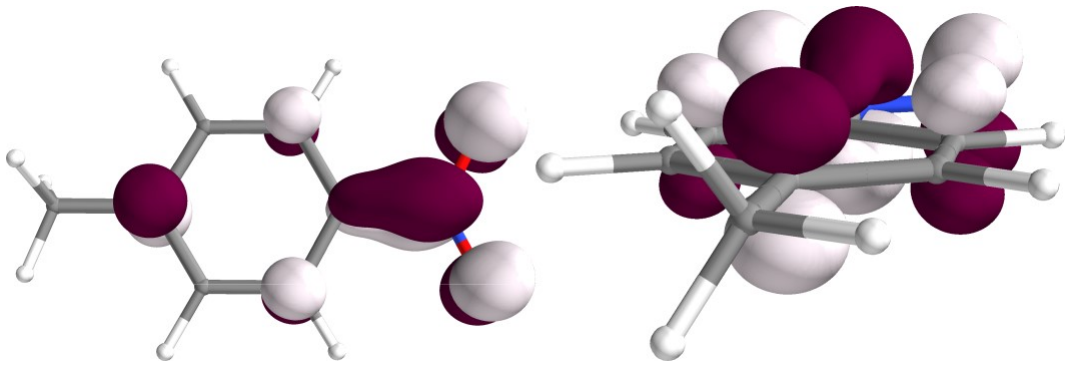
Total molecular energy	-475.67528 hartrees
HOMO number	36
LUMO+1 energies	-0.94 eV
LUMO energies	-2.45 eV
HOMO energies	-7.87 eV
HOMO-1 energies	-8.05 eV
Geometry optimization specific results	
Converged nuclear repulsion energy	495.04708 Hartrees
Frequency and Thermochemistry specific results	
Enthalpy at 298.15 K	-475.53552 Hartrees

Gibbs free energy at 298.15 K -475.57752 Hartrees

Entropy at 298.15 K 0.00014 Hartrees



Representation of the HOMO from two points of view.



Representation of the LUMO from two points of view.

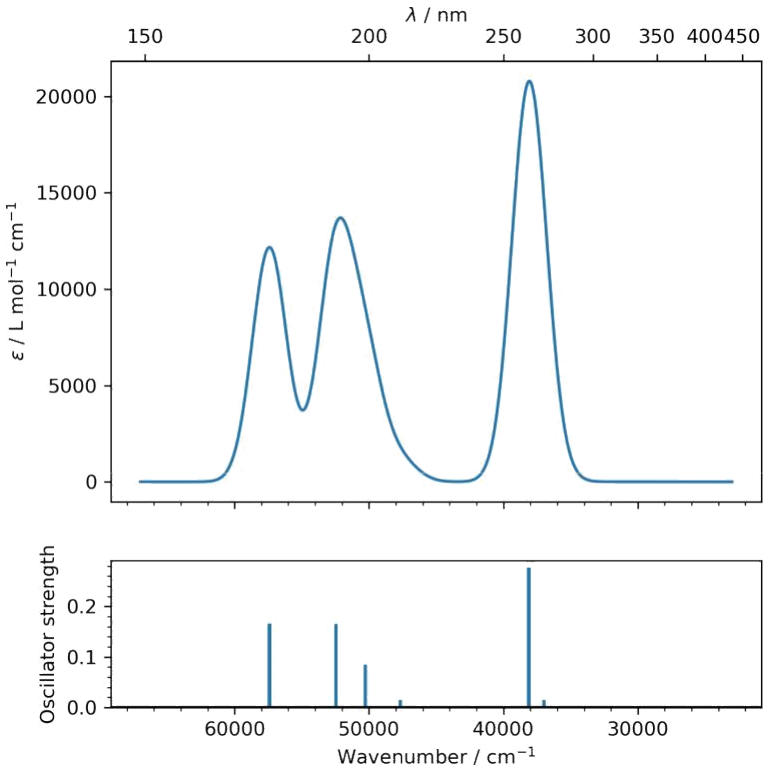
Results concerning the calculated mono-electronic excitations.

E.S.	Symmetry	nm	$_{cm}$−1	*f*	R	Λ	d*CT*	q*CT*	Excitation description : initial OM - ending OM (% if > 5%)
1	Singlet-A	312	31967	0.000	-0.1	0.46	174.78	0.77	34-37(95);
2	Singlet-A	276	36125	0.000	0.1	0.52	161.99	0.72	33-37(95);
3	Singlet-A	270	36993	0.015	-0.1	0.53	267.06	0.65	35-37(89); 36-38(7);
4	**Singlet-A**	**262**	**38115**	**0.277**	**0.1**	**0.63**	**316.82**	**0.63**	**36-37(93);**
5	Singlet-A	209	47678	0.015	-0.0	0.64	29.02	0.36	32-37(8); 35-37(6); 35-39(15); 36-38(66);
6	Singlet-A	198	50266	0.085	-0.0	0.66	226.69	0.49	32-37(84); 35-39(6);
7	Singlet-A	190	52465	0.165	-0.0	0.81	28.60	0.25	35-38(68); 36-39(26);
8	Singlet-A	188	53031	0.000	0.0	0.22	204.67	0.75	31-37(30); 34-38(68);
9	Singlet-A	188	53068	0.000	0.0	0.28	78.76	0.68	31-37(66); 34-38(31);
10	Singlet-A	179	55606	0.000	-0.0	0.27	213.75	0.80	36-40(97);

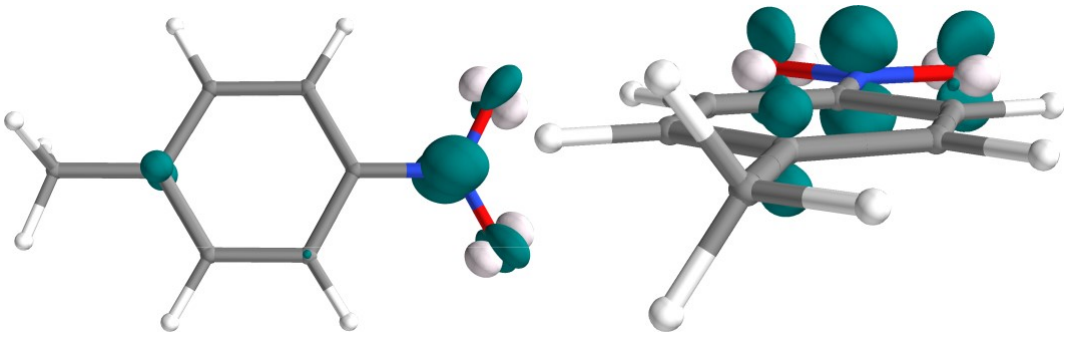
11	Singlet-A	178	55912	0.000	-0.0	0.18	330.98	0.93	33-38(98);
12	Singlet-A	175	56944	0.000	0.0	0.26	228.87	0.81	35-40(93);
13	Singlet-A	174	57403	0.166	0.2	0.39	323.17	0.63	32-38(64); 35-38(8); 36-39(23);
14	Singlet-A	173	57635	0.000	-0.1	0.30	318.06	0.84	34-39(92);
15	Singlet-A	172	57825	0.002	0.0	0.39	356.88	0.76	30-37(91);

Converged cartesian atomic coordinates in Angstroms

Atom	X	Y	Z
C	-0.0473	1.2100	-0.0002
C	-0.7191	0.0010	-0.0000
C	-0.0424	-1.2083	0.0001
C	1.3396	-1.1958	0.0001
C	2.0522	0.0051	-0.0000
C	1.3376	1.2012	-0.0002
N	-2.1817	-0.0013	0.0000
O	-2.7431	-1.0803	-0.0003
O	-2.7472	1.0753	0.0004
H	-0.6039	-2.1314	0.0003
H	1.8784	-2.1359	0.0001
C	3.5504	-0.0012	0.0000
H	1.8741	2.1423	-0.0003
H	-0.6107	2.1320	-0.0003
H	3.9537	1.0105	-0.0010
H	3.9387	-0.5197	0.8793
H	3.9389	-0.5216	-0.8781

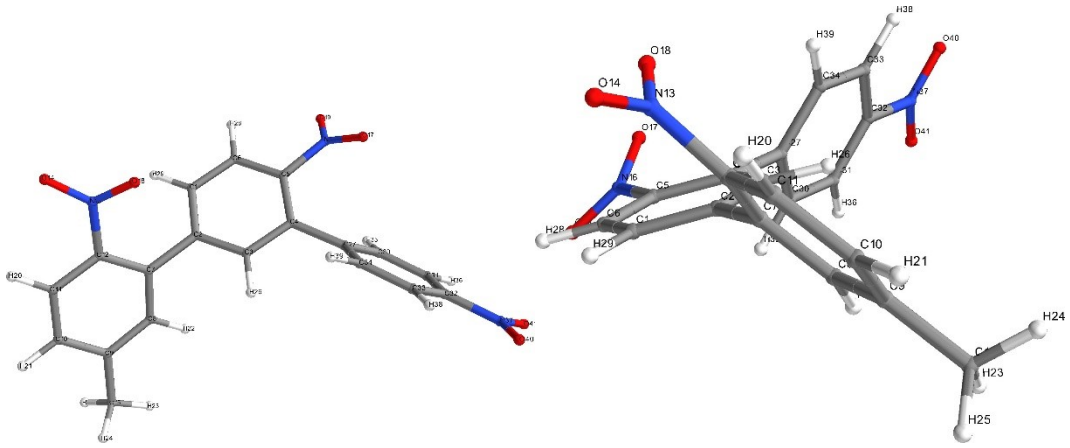


Calculated UV visible Absorption spectrum with a gaussian broadening (FWHM = 3000 cm-1)



Representation of the Electron Density Difference (S1-S0) from two points of view.

- **MOLECULE**

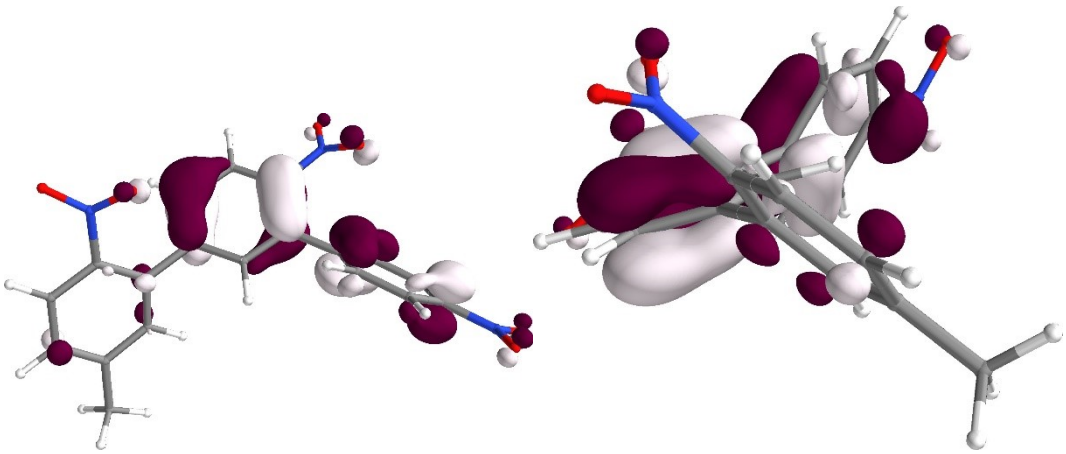


Chemical structure diagram with atomic numbering from two points of view.

Formula	C19H13N3O6
Charge	0
Spin multiplicity	1

- **RESULTS**

Total molecular energy	-1346.07158 hartrees
HOMO number	98
LUMO+1 energies	-2.70 eV
LUMO energies	-2.93 eV
HOMO energies	-7.82 eV
HOMO-1 energies	-7.96 eV
Geometry optimization specific results	
Converged nuclear repulsion energy	2434.97435 Hartrees
Frequency and Thermochemistry specific results	
Enthalpy at 298.15 K	-1345.74901 Hartrees
Gibbs free energy at 298.15 K	-1345.83294 Hartrees
Entropy at 298.15 K	0.00028 Hartrees

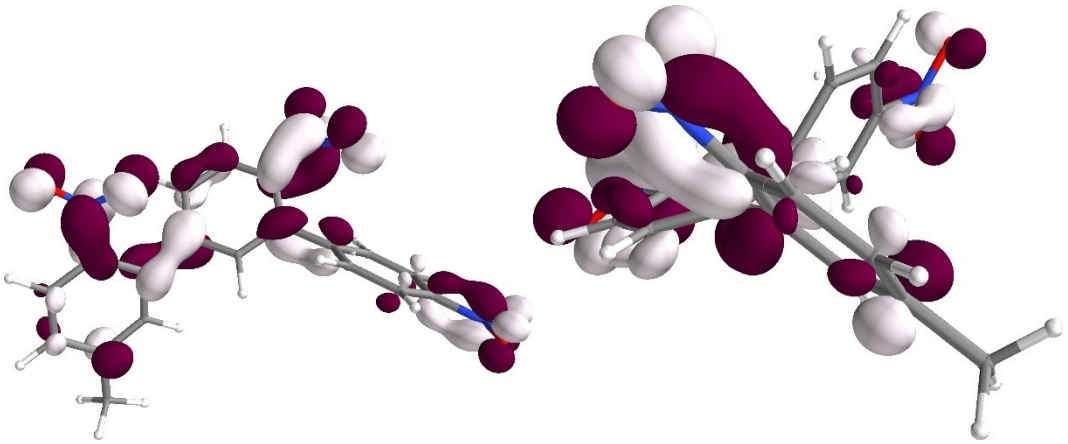


Representation of the HOMO from two points of view.

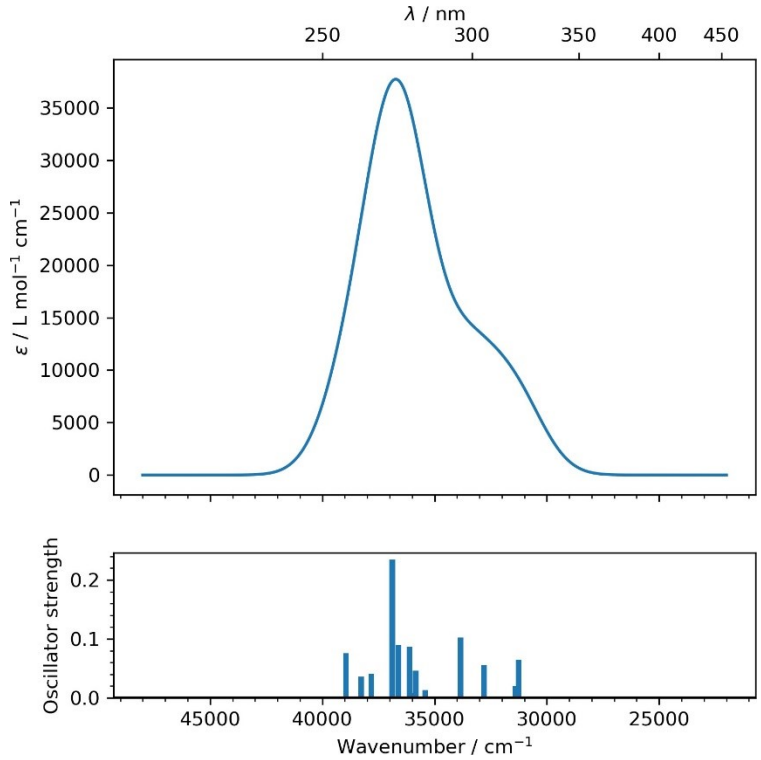
Results concerning the calculated mono-electronic excitations.

E.S.	Symmetry	nm	cm^{-1}	*f*	R	Λ	d*CT*	q*CT*	Excitation description : initial OM - ending OM (% if > 5%)
1	Singlet-A	319	31254	0.065	-117.9	0.48	261.86	0.44	91-101(10); 93-99(7); 96-99(8); 97-99(20); 97-101(7);
2	Singlet-A	318	31403	0.020	-42.7	0.43	399.52	0.52	88-100(7); 91-99(15); 91-100(9); 96-99(13); 96-100(19);
3	Singlet-A	315	31679	0.002	19.1	0.44	504.11	0.62	92-99(16); 92-100(28); 92-101(20); 93-100(10); 93-101(8);
4	Singlet-A	304	32789	0.056	-82.1	0.59	122.54	0.55	98-99(78);
5	Singlet-A	295	33836	0.102	15.1	0.51	118.80	0.52	97-99(30); 97-100(10); 98-100(26); 98-101(10);
6	Singlet-A	282	35424	0.013	12.2	0.47	184.75	0.40	87-99(10); 87-101(9); 93-99(9); 94-99(11); 97-99(7);
7	Singlet-A	279	35760	0.001	17.4	0.30	690.02	0.73	90-99(21); 90-100(37); 90-101(26);
8	Singlet-A	279	35840	0.046	126.3	0.42	243.37	0.39	88-99(6); 88-100(8); 94-99(9); 94-100(7); 95-99(7); 98-100(6);
9	Singlet-A	278	35902	0.008	6.0	0.38	318.27	0.52	95-99(41); 95-100(9); 97-99(6); 98-100(12);

10	Singlet-A	276	36118	0.087	72.7	0.41	198.11	0.47	95-99(12); 97-99(7); 98-100(40);
11	Singlet-A	273	36614	0.090	-54.4	0.50	176.92	0.56	97-100(16); 97-101(6); 98-99(7); 98-101(54);
12	Singlet-A	271	36885	0.234	39.1	0.47	246.85	0.48	96-99(12); 97-99(12); 97-100(34); 98-101(17);
13	Singlet-A	264	37814	0.041	-66.0	0.46	312.84	0.51	95-99(8); 96-99(34); 97-100(19); 97-101(7);
14	Singlet-A	261	38269	0.036	-10.3	0.39	215.21	0.68	95-99(10); 95-100(22); 95-101(42); 96-99(6);
15	Singlet-A	256	38943	0.076	28.5	0.46	341.30	0.49	97-101(61);



Representation of the LUMO from two points of view.



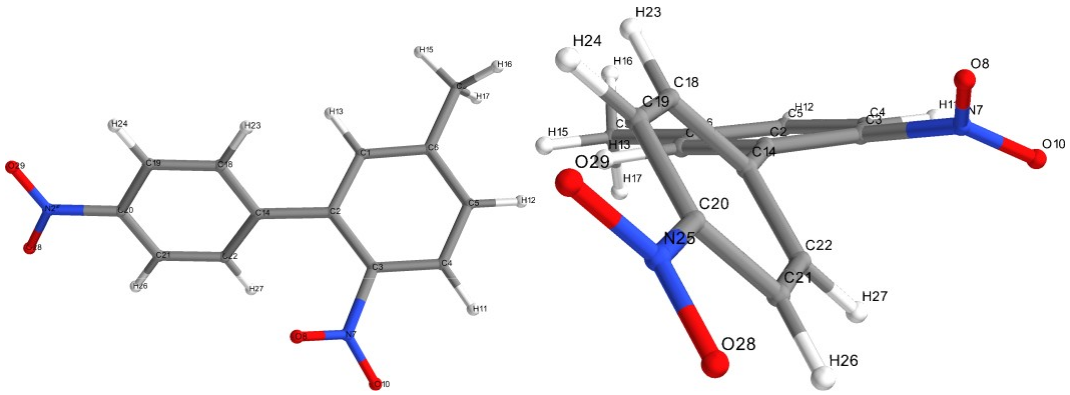
Calculated UV visible Absorption spectrum with a gaussian broadening (FWHM = 3000 cm-1)

Converged cartesian atomic coordinates in Angstroms

Atom	X	Y	Z
C	1.8828	-1.7877	-0.6920
C	1.7224	-0.4581	-0.3081
C	0.4390	0.0332	-0.0970
C	-0.6946	-0.7677	-0.2201
C	-0.4859	-2.0972	-0.5861
C	0.7786	-2.6020	-0.8404
C	2.8860	0.4539	-0.2093
C	2.9237	1.5787	-1.0325
C	4.0011	2.4575	-1.0557
C	5.0945	2.1839	-0.2348
C	5.0965	1.0746	0.5865
C	3.9949	0.2339	0.6071
N	4.0261	-0.8666	1.5728
O	5.1129	-1.3470	1.8314
C	3.9976	3.6597	-1.9494
N	-1.5988	-3.0478	-0.6693
O	-2.5123	-2.9144	0.1182
O	2.9726	-1.2113	2.0698
O	-1.5164	-3.9222	-1.5106
H	5.9338	0.8516	1.2329
H	5.9506	2.8477	-0.2366

H	2.0845	1.7539	-1.6954
H	3.0770	3.7265	-2.5275
H	4.0989	4.5774	-1.3664
H	4.8356	3.6282	-2.6489
H	0.3064	1.0740	0.1714
C	-2.0232	-0.1442	-0.0207
H	0.8782	-3.6365	-1.1374
H	2.8719	-2.1858	-0.8793
C	-2.9772	-0.1529	-1.0386
C	-4.1908	0.4869	-0.8722
C	-4.4423	1.1360	0.3247
C	-3.5166	1.1630	1.3523
C	-2.3033	0.5230	1.1708
H	-2.7656	-0.6578	-1.9728
H	-4.9405	0.4936	-1.6500
N	-5.7255	1.8190	0.5068
H	-3.7566	1.6755	2.2726
H	-1.5724	0.5218	1.9693
O	-5.9170	2.3810	1.5676
O	-6.5166	1.7827	-0.4152

- **MOLECULE**



Chemical structure diagram with atomic numbering from two points of view.

Formula	C13H10N2O4
Charge	0
Spin multiplicity	1

RESULTS

Total molecular energy	-910.87343 hartrees
HOMO number	67
LUMO+1 energies	-2.46 eV
LUMO energies	-2.77 eV
HOMO energies	-7.75 eV
HOMO-1 energies	-8.03 eV

Geometry optimization specific results

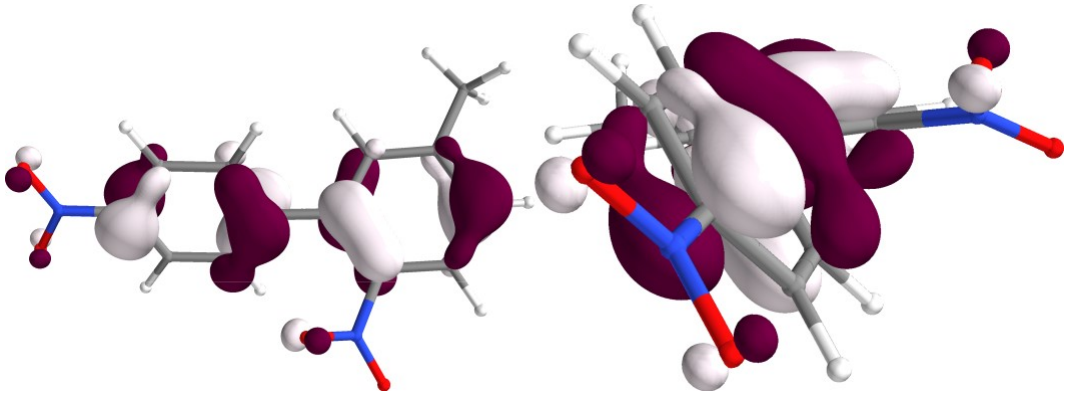
Converged nuclear repulsion energy 1346.30750 Hartrees

Frequency and Thermochemistry specific results

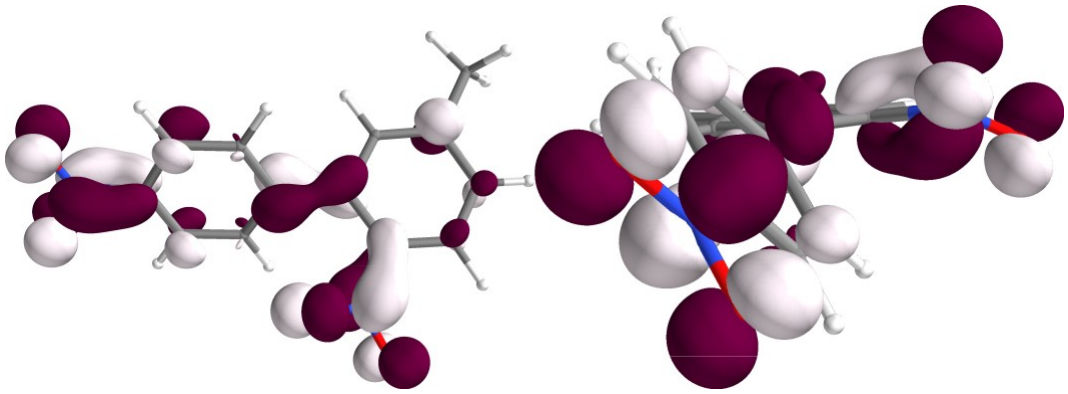
Enthalpy at 298.15 K -910.64175 Hartrees

Gibbs free energy at 298.15 K -910.70521 Hartrees

Entropy at 298.15 K 0.00021 Hartrees



Representation of the HOMO from two points of view.

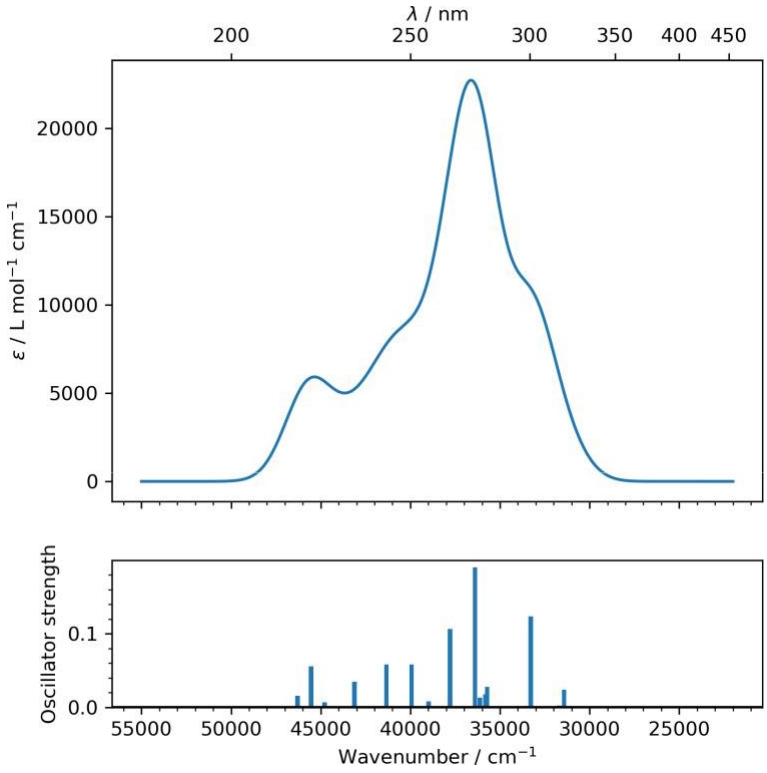


Representation of the LUMO from two points of view.

Results concerning the calculated mono-electronic excitations.

E.S.	Symmetry	nm	$_{cm}$−1	*f*	R	Λ	d*CT*	q*CT*	Excitation description : initial OM - ending OM (% if > 5%)
1	Singlet-A	318	31418	0.024	-67.1	0.49	383.89	0.57	62-68(16); 62-69(17); 66-68(27); 66-69(21);
2	Singlet-A	315	31691	0.002	18.8	0.47	380.11	0.64	63-68(46); 63-69(27); 64-68(9); 64-69(7);
3	Singlet-A	300	33280	0.124	-65.2	0.60	223.58	0.59	67-68(75); 67-69(17);

4	Singlet-A	279	35719	0.028	59.7	0.51	12.53	0.44	59-68(8); 59-69(8); 61-68(15); 61-69(7); 64-68(10); 64-69(7); 65-68(10);
5	Singlet-A	279	35805	0.018	12.3	0.42	368.20	0.56	61-68(38); 61-69(25);
6	Singlet-A	276	36124	0.013	30.7	0.49	77.36	0.58	65-68(67);
7	Singlet-A	274	36391	0.190	-11.4	0.54	221.05	0.58	66-68(7); 67-68(16); 67-69(61);
8	Singlet-A	264	37786	0.106	0.2	0.50	387.84	0.54	65-68(7); 66-68(46); 66-69(14); 67-69(8);
9	Singlet-A	256	38978	0.009	5.2	0.42	163.87	0.76	65-69(87);
10	Singlet-A	250	39932	0.058	9.6	0.51	348.60	0.51	62-68(10); 64-68(10); 66-69(50);
11	Singlet-A	241	41335	0.058	45.0	0.55	191.43	0.47	62-68(7); 63-68(6); 64-68(41);
12	Singlet-A	231	43119	0.035	-11.2	0.52	151.45	0.49	59-68(7); 62-68(8); 64-69(53);
13	Singlet-A	223	44783	0.007	-2.2	0.46	399.82	0.66	63-68(31); 63-69(49); 64-68(6);
14	Singlet-A	219	45538	0.056	10.1	0.56	202.29	0.39	66-70(6); 67-70(54); 67-71(8);
15	Singlet-A 215 46300 0.0166.8 0.51 294.53 0.47 62-68(22); 62-69(29); 66-70(15); 67-70(10); 67-71(7);								



Calculated UV visible Absorption spectrum with a gaussian broadening (FWHM = 3000 cm-1)

Converged cartesian atomic coordinates in Angstroms

Atom	X	Y	Z
C	-1.9084	-1.4771	-0.1173

C	-1.2697	-0.2455	0.0270
C	-2.0884	0.8815	0.0932
C	-3.4677	0.7919	-0.0085
C	-4.0645	-0.4455	-0.1422
C	-3.2907	-1.6043	-0.1926
N	-1.5347	2.2157	0.3342
O	-0.5479	2.2982	1.0370
C	-3.9357	-2.9485	-0.3399
O	-2.1191	3.1575	-0.1674
H	-4.0531	1.6995	0.0379
H	-5.1439	-0.5133	-0.2048
H	-1.2908	-2.3638	-0.1994
C	0.2110	-0.2154	0.0213
H	-3.1953	-3.7466	-0.3692
H	-4.6150	-3.1469	0.4918
H	-4.5257	-2.9999	-1.2574
C	0.9252	-0.9993	0.9262
C	2.3079	-1.0351	0.8933
C	2.9691	-0.2852	-0.0627
C	2.2881	0.4983	-0.9792
C	0.9075	0.5293	-0.9311
H	0.3926	-1.5706	1.6758
H	2.8782	-1.6282	1.5935
N	4.4323	-0.3256	-0.1100
H	2.8433	1.0649	-1.7125
H	0.3637	1.1312	-1.6483
O	4.9853	0.3388	-0.9645
O	5.0018	-1.0230	0.7070