Supplementary Materials

Article

Trifluoromethyl substituted derivatives of pyrazoles as materials for photovoltaic and electroluminescent applications

Monika Pokladko-Kowar[1]*, Ewa Gondek[1], Andrzej Danel[1]*, Tomasz Uchacz[2], Paweł Szlachcic[3], Katarzyna Wojtasik[1]*, Paweł Karasiński[4]

1 Department of Physics, Cracow University of Technology, Podchorążych Str.1, 30-084, Kraków, Poland; e.gondek@wp.pl (E.G.); mpokladkokowar@pk.edu.pl (M.P.-K.); rrdanela@cyf-kr.edu.pl (A.D.); katarzyna.wojtasik@pk.edu.pl (K.W.)
2 Faculty of Chemistry, Jagiellonian University, Gronostajowa Str.2, Kraków, 30-387, Poland; uchacz@chemia.uj.edu.pl (T.U.)
3 Faculty of Food Technology, Agricultural University, Balicka Str. 122, Kraków, 31-149, Poland; pawel.szlachcic@urk.edu.pl (P.S.)
4 Department of Optoelectronics, Silesian University of Technology, B. Krzywoustego 2, 44-100 Gliwice, Poland; pawel.karasinski@polsl.pl (P.K.)
* Correspondence: mpokladkokowar@pk.edu.pl (M.P.-K.); rrdanela@cyf-kr.edu.pl (A.D.); katarzyna.wojtasik@pk.edu.pl (K.W.)

Table of contents

Figure S1. Tauc plots prepared for the studied compounds.

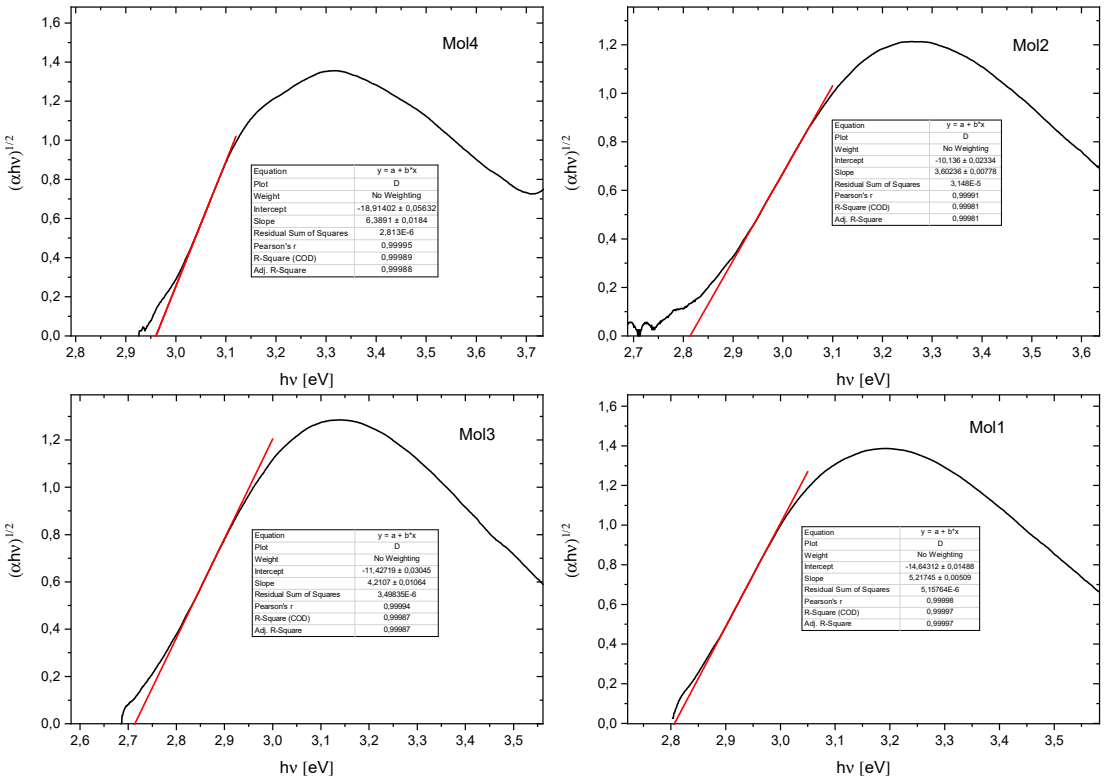


Figure S2. Energy changes vs dihedral angle changes of phenyl substituent and the pyrazoloquinoline core for **Mol1** (red) and for **Mol2** (blue).

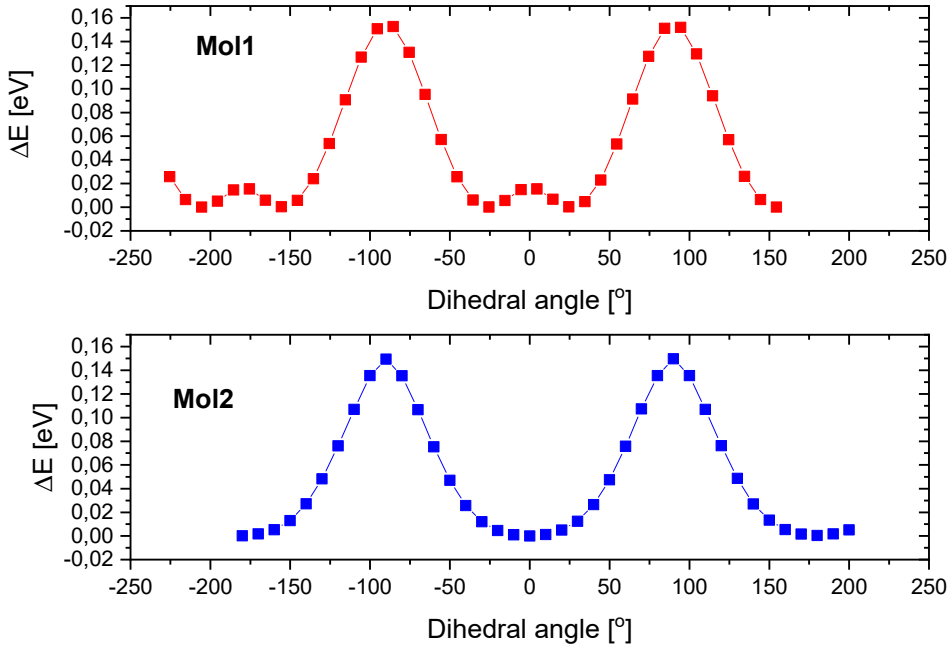


Figure S3. Molecular structures of two possible rotamers of **Mol1** (dihedral angle of phenyl substituent and the pyrazoloquinoline core: 24˚ and 60˚) and **Mol2** (dihedral angle of phenyl substituent and the pyrazoloquinoline core: 0˚ and 60˚).

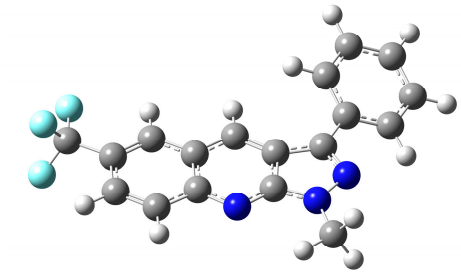
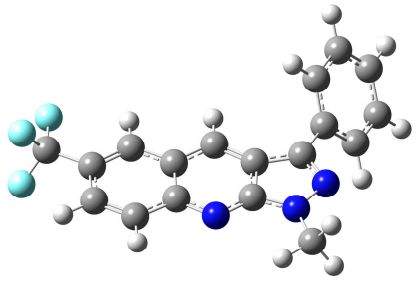
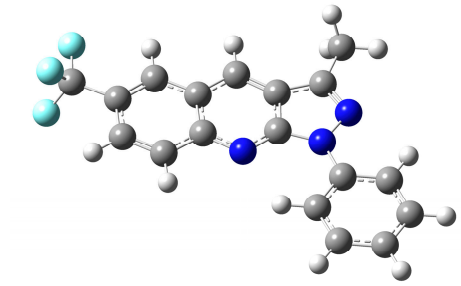
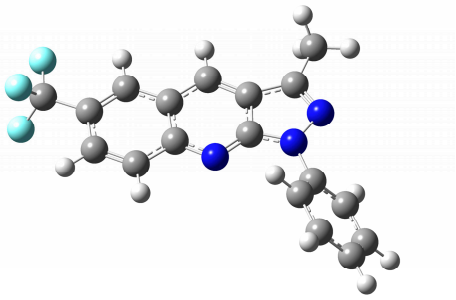
Rotamer 1 of **Mol1$_p$**	Rotamer 2 of **Mol1$_t$**
	
Rotamer 1 of **Mol2$_p$**	Rotamer 2 of **Mol2$_t$**
	

Figure S4. Figure S13. Simulated TDDFT (B3LYP/cc-pVDZ with a continuum solvent model for acetonitrile) and averaged UV-vis absorption spectra of **Mol2** and **Mol1**. No spectral shift has been applied. For calculated structures see **Figure S3**. For the excitation assignment see **Table S1**.

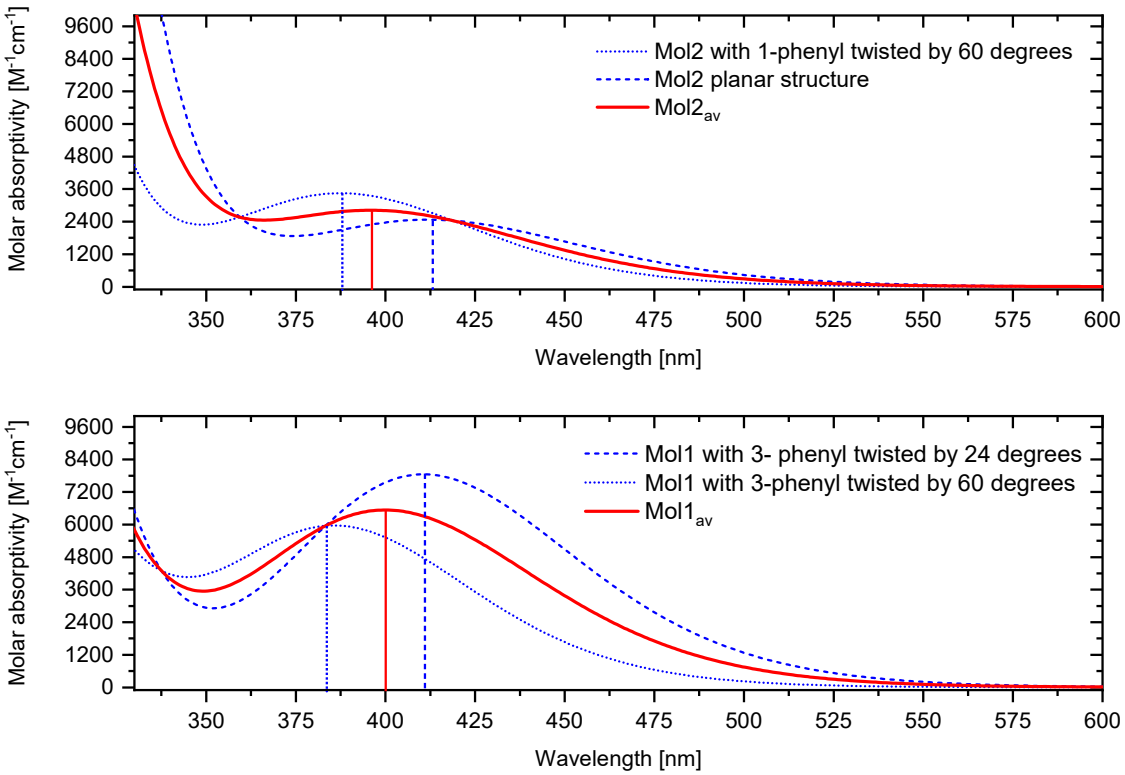


Table S1. Lowest-energy excitation and its characteristics calculated (B3LYP/cc-pVDZ with a continuum solvent model for acetonitrile (ACN)) for the studied molecules.

Compound	λ/nm	E/eV	f	ε [$M^{-1}cm^{-1}$]	Contribution	%
Mol4	382	3.24	0.099	4100	H→L	97
$Mol1_p$	411	3.02	0.194	7850	H→L	98
$Mol1_t$	387	3.21	0.146	6000	H→L	97
$Mol2_p$	413	3.01	0.096	2450	H→L	99
$Mol2_t$	388	3.19	0.085	3450	H→L	98
Mol3	434	2.86	0.162	6550	H→L	99

Figure S5. Isosurfaces (±0.03 au) of MOs involved in the lowest-energy excitations for the most populated conformers of the studied compounds B3LYP/cc-pVDZ calculations with a continuum solvent model for acetonitrile.

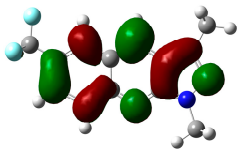
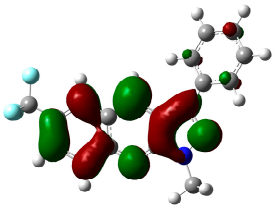
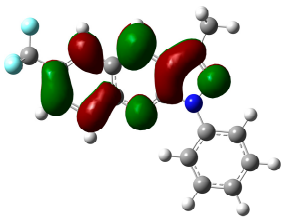
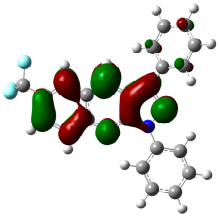
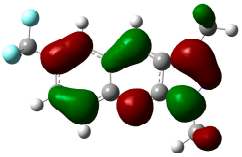
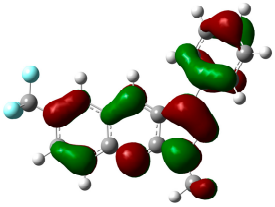
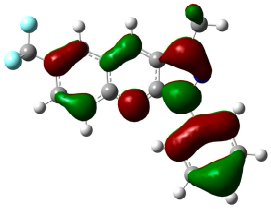
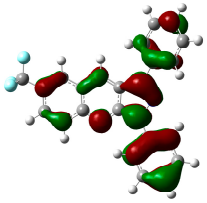
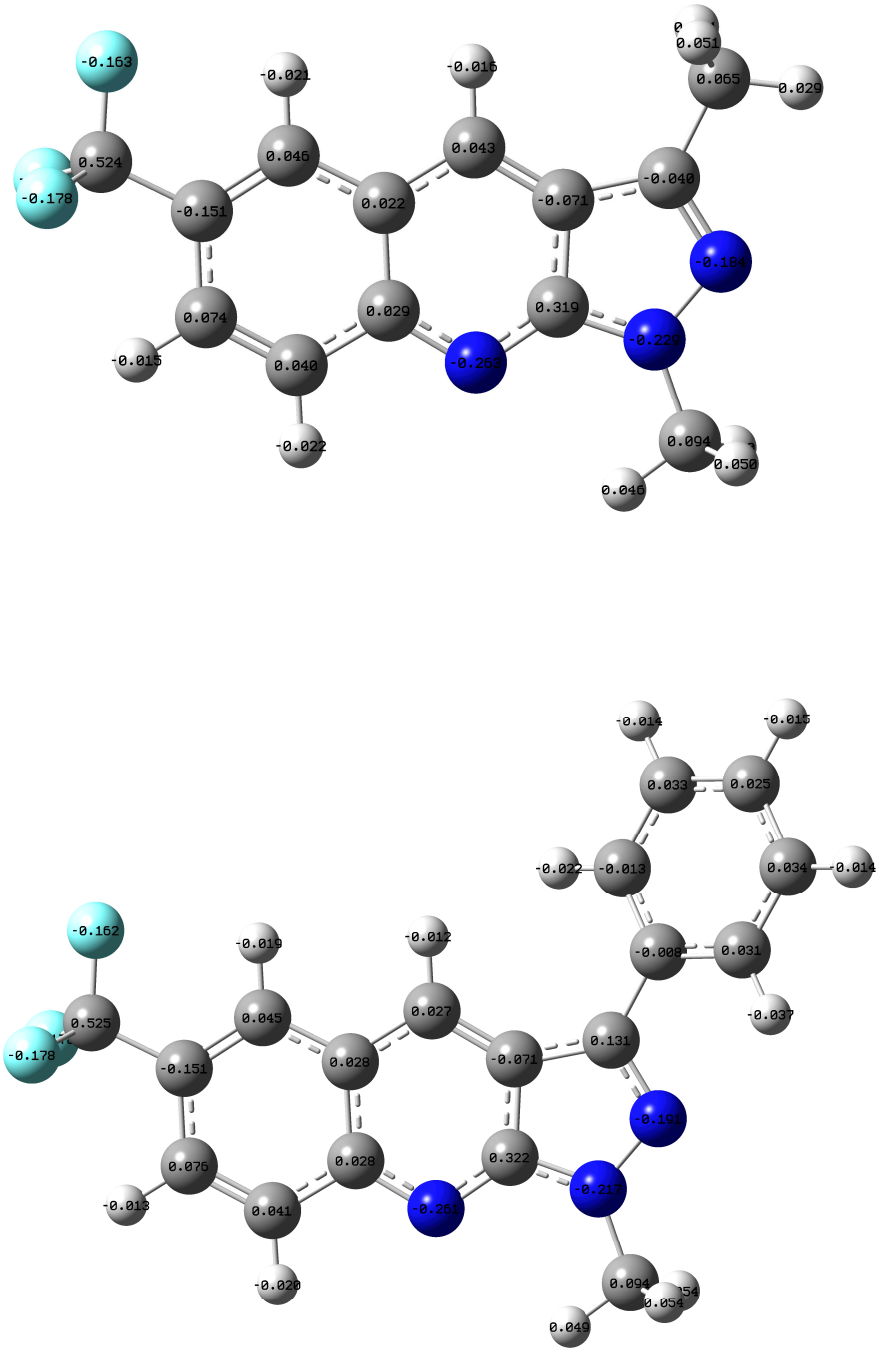
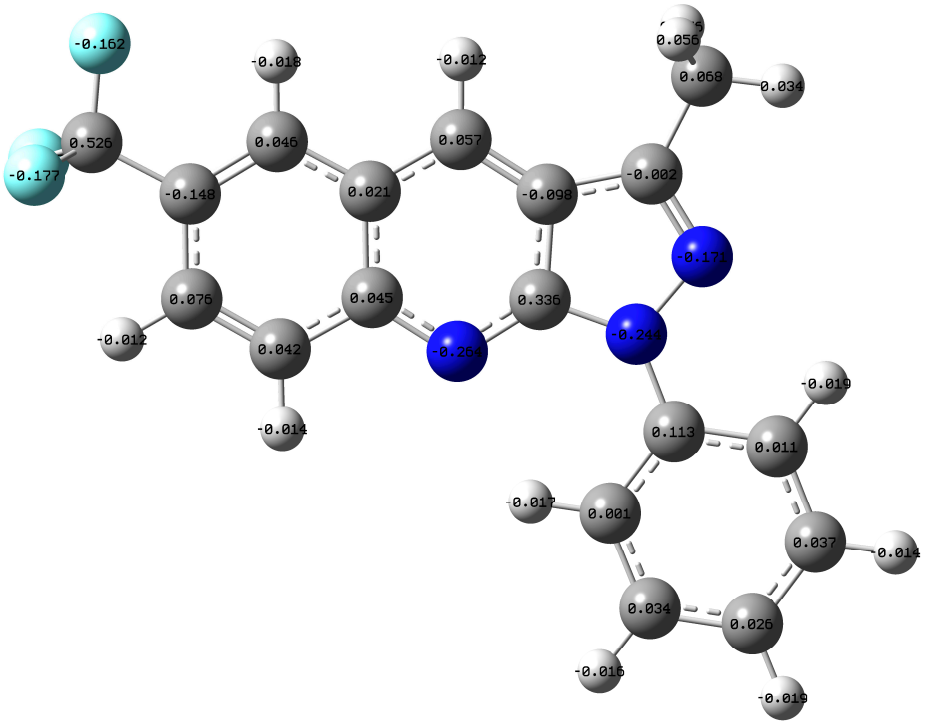
	Mol4	Mol1	Mol2	Mol3
LUMO				
HOMO				

Figure S6. Charges located at the atoms of each studied compound.




-0.162
-0.018
-0.012
0.056
0.068
-0.034
0.526
0.046
0.057
-0.177
-0.148
0.021
-0.098
-0.002
-0.171
0.076
0.045
0.336
-0.012
-0.244
0.042
-0.264
-0.019
-0.014
0.113
0.011
-0.017
0.001
0.037
-0.014
0.034
0.026
-0.016
-0.019

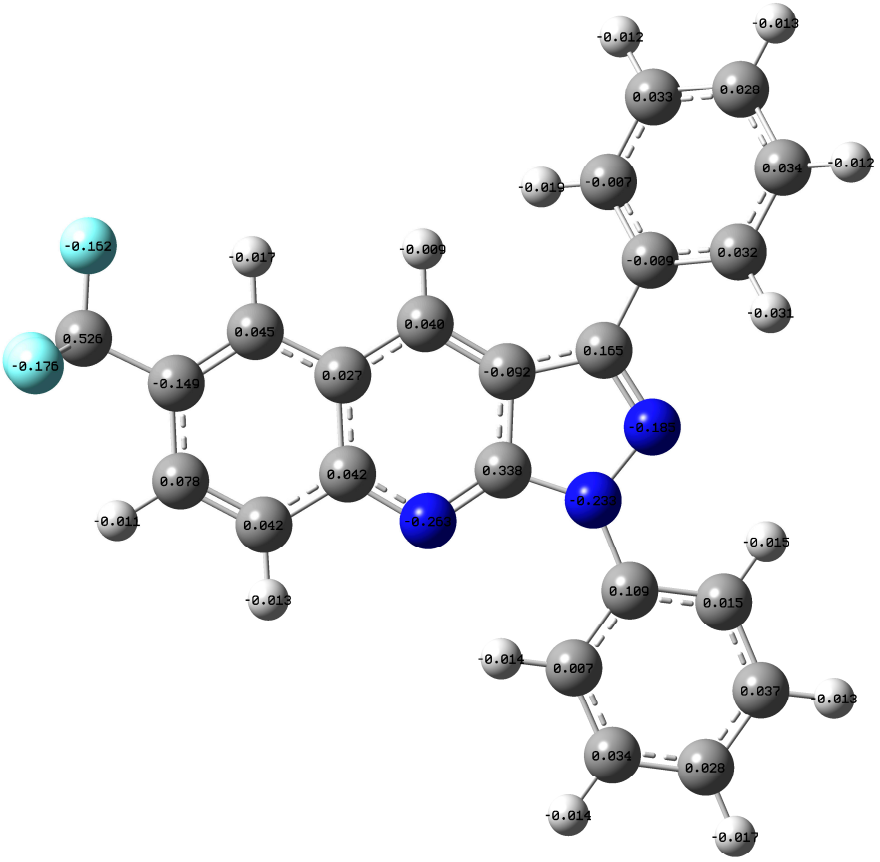

-0.012
-0.013
0.033
0.028
0.034
-0.012
-0.010
-0.007
-0.162
-0.017
-0.009
-0.009
0.032
-0.031
0.526
0.045
0.040
0.165
-0.176
-0.149
0.027
-0.092
-0.185
0.078
0.042
0.338
-0.011
-0.238
0.042
-0.263
-0.015
-0.013
0.109
0.015
-0.014
0.007
0.037
-0.013
0.034
0.028
-0.014
-0.017

Table S2. Oxidation potentials and HOMO/LUMO energy levels of the investigated dyes. Energy band gap was evaluated by means of Tauc equation.

Compound	E_{ox} [V]	HOMO [eV]	Band gap [eV]	LUMO [eV]
Mol4	1.268	-6.375	2.960	-3.415
Mol2	1.104	-6.146	2,813	-3.333
Mol1	1.196	-6.274	2,810	-3.464
Mol3	1.093	-6.130	2,713	-3.417

Table S3. Optimized (B3LYP/cc-pVDZ with a continuum solvent model for acetonitrile) ground-state geometries of **Mol1**, **Mol2**, **Mol3**, **Mol4** along with the corresponding absolute energies. The atomic symbol followed by three Cartesian coordinates, in Å.

Mol4
E=-965.267931 a.u.
G= -965.100907 a.u.

Symbol	X	Y	Z
N	-1.3725640	-1.5438150	0.0000030
C	-0.1105690	-1.0418380	0.0000040
C	0.1857550	0.3755040	0.0000040
C	-0.8830210	1.3045360	0.0000030
C	-2.1702050	0.7990200	0.0000020
C	-2.3314470	-0.6287320	0.0000030
C	1.5461410	0.7994030	0.0000040
C	2.5687390	-0.1208540	0.0000050
C	2.2831450	-1.5191180	0.0000070
C	0.9837310	-1.9611190	0.0000060
C	-3.5162840	1.3154390	0.0000010
N	-4.3818000	0.3176960	0.0000000
N	-3.6774610	-0.8568970	0.0000020
H	-0.6783330	2.3776520	0.0000020
H	1.7635080	1.8683440	0.0000060
H	3.1052880	-2.2367200	0.0000100
H	0.7491010	-3.0267070	0.0000080
C	4.0041370	0.3150360	-0.0000030
F	4.1478850	1.6584590	0.0000240
F	4.6753370	-0.1541310	1.0838410
F	4.6753090	-0.1540820	-1.0838820
C	-3.9608160	2.7420840	0.0000000
H	-3.5823440	3.2765060	0.8870070
H	-3.5823310	3.2765100	-0.8869980
H	-5.0580400	2.7958550	-0.0000070
C	-4.3641920	-2.1325560	-0.0000120
H	-3.6022700	-2.9217290	0.0000220
H	-4.9946700	-2.2308190	0.8967290
H	-4.9946080	-2.2308350	-0.8967950

Mol1
E= -1157.021298 a.u.
G= -1156.805223 a.u.

Symbol	X	Y	Z
N	-0.3678810	2.3999070	0.0649900
C	-1.3825750	1.4993140	0.0407310
C	-1.1715260	0.0686750	0.0005090
C	0.1498440	-0.4375930	0.0010570
C	1.1924080	0.4738000	0.0489640
C	0.8450580	1.8686430	0.0626350
C	-2.3026810	-0.7978630	-0.0382170
C	-3.5786810	-0.2852150	-0.0322100
C	-3.7926470	1.1255370	0.0118410
C	-2.7256650	1.9876780	0.0466520
C	2.6396580	0.4669800	0.0448260
N	3.0923740	1.7151500	0.0468880
N	2.0267310	2.5566760	0.0570310
C	3.5771130	-0.6689840	0.0164840
C	4.8740630	-0.5001310	-0.5081570
C	5.7756070	-1.5641360	-0.5329770
C	5.4012130	-2.8196070	-0.0375690
C	4.1188120	-2.9973160	0.4902790
C	3.2144430	-1.9319550	0.5205980
H	5.1616630	0.4756700	-0.9019660
H	6.7753490	-1.4155240	-0.9473860
H	6.1063620	-3.6532360	-0.0619500
H	3.8197830	-3.9690540	0.8893300
H	2.2303910	-2.0811480	0.9667010
H	0.3131260	-1.5155080	-0.0436460
H	-2.1391070	-1.8756940	-0.0704740
H	-4.8117760	1.5153960	0.0170120
H	-2.8718230	3.0684240	0.0786190
C	-4.7765860	-1.1881970	-0.0713720
F	-4.4485540	-2.4982750	-0.1019030
F	-5.5811570	-1.0065000	1.0075040
F	-5.5535970	-0.9494440	-1.1593640
C	2.2158510	3.9942210	0.0856910
H	1.2236710	4.4609040	0.0680170
H	2.7482090	4.2933910	1.0011040
H	2.7930980	4.3191350	-0.7924430

Mol2
E=-1157.021922 a.u.
G= -1156.806538 a.u.

Mol3
E= -1348.774156 a.u.
G= -1348.510042 a.u.

Symbol	X	Y	Z
N	-0.5499690	-0.7381370	-0.0000010
C	0.8034920	-0.5963950	0.0000000
C	1.4703630	0.6848060	0.0000020
C	0.6864160	1.8635010	0.0000020
C	-0.6865860	1.7178270	0.0000000
C	-1.2369580	0.3929760	-0.0000020
C	2.8939580	0.7287080	0.0000030
C	3.6290270	-0.4342530	0.0000010
C	2.9765490	-1.7022990	0.0000000
C	1.6053070	-1.7776770	0.0000000
C	-1.8292990	2.5967990	-0.0000010
N	-2.9390560	1.8943980	-0.0000010
N	-2.6113880	0.5524850	0.0000000
C	-3.6570680	-0.4097200	0.0000010
C	-3.3776070	-1.7871660	0.0000010
C	-4.4329570	-2.7038480	0.0000010
C	-5.7623200	-2.2723050	0.0000000
C	-6.0313650	-0.8992170	-0.0000010
C	-4.9920770	0.0320790	0.0000000
H	-2.3447310	-2.1262060	0.0000020
H	-4.2036520	-3.7719330	0.0000020
H	-6.5795960	-2.9962960	0.0000000
H	-7.0637160	-0.5420610	-0.0000020
H	-5.1991130	1.1001650	-0.0000010
H	1.1651140	2.8451440	0.0000030
H	3.3908570	1.6995910	0.0000040
H	3.5739890	-2.6153720	0.0000000
H	1.0940900	-2.7414250	-0.0000010
C	5.1299030	-0.4027150	0.0000000
F	5.6301450	0.8518670	0.0000130
F	5.6472000	-1.0356780	1.0839950
F	5.6471970	-1.0356540	-1.0840110
C	-1.8431020	4.0899350	0.0000000
H	-1.3241010	4.4881640	0.8871410
H	-1.3241100	4.4881630	-0.8871470
H	-2.8770790	4.4598030	0.0000050

Symbol	X	Y	Z
N	0.2192940	-1.6736640	0.0158300
C	1.4887180	-1.1874180	0.0139860
C	1.7954730	0.2228950	-0.0052950
C	0.7325890	1.1561350	-0.0041370
C	-0.5600310	0.6640300	0.0240960
C	-0.7372490	-0.7606680	0.0157570
C	3.1582720	0.6384600	-0.0245820
C	4.1713030	-0.2916680	-0.0183740
C	3.8739760	-1.6867920	0.0064570
C	2.5708660	-2.1188050	0.0215090
C	-1.9030650	1.2013480	0.0156100
N	-2.7801450	0.2148010	-0.0025750
N	-2.1049480	-0.9772950	-0.0031700
C	-2.8489180	-2.1905330	0.0230610
C	-2.2235020	-3.4297960	-0.1920310
C	-2.9882210	-4.5996290	-0.1639860
C	-4.3653870	-4.5534060	0.0697700
C	-4.9798540	-3.3142230	0.2810420
C	-4.2329470	-2.1356070	0.2617270
C	-2.3512080	2.6048270	-0.0052400
C	-3.5814620	2.9431180	-0.6021420
C	-4.0217080	4.2666570	-0.6185090
C	-3.2423470	5.2772220	-0.0417770
C	-2.0217730	4.9513540	0.5574200
C	-1.5786330	3.6260880	0.5781870
H	-1.1520210	-3.4698530	-0.3699700
H	-2.4926370	-5.5584520	-0.3318480
H	-4.9544460	-5.4724950	0.0881200
H	-6.0546680	-3.2589200	0.4674820
H	-4.7083300	-1.1711120	0.4285110
H	-4.1818790	2.1564770	-1.0611650
H	-4.9757490	4.5130640	-1.0898000
H	-3.5862740	6.3136150	-0.0590760
H	-1.4118750	5.7308140	1.0190730
H	-0.6401520	3.3847020	1.0789590
H	0.9495820	2.2248570	-0.0313610
H	3.3839190	1.7053240	-0.0419880
H	4.6900330	-2.4111040	0.0123590
H	2.3291110	-3.1824100	0.0387440
C	5.6119240	0.1314420	-0.0366790
F	5.7661370	1.4728640	-0.0595640
F	6.2847820	-0.3268270	1.0495380
F	6.2674220	-0.3617690	-1.1181800