PM3 study of some newly synthesis compounds incorporating simultaneously two deferent heterocyclic rings :1,3,4-oxadiazole and 1,3,4-thiadiazole

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Abstract

The PM3 semi empirical MO method within the Gaussian 03 program was used to study twelve newly synthesis compounds(1-12) along with the parent compound,1, incorporating two heterocyclic 1,3,4-oxadiazole and 1,3,4-thiadiazole rings were studied theoretically using . The geometric parameters, dipole moments, electron densities, HOMO and LUMO energies and thermodynamics data U^o, H^o, S^o, G^o, and A^o of these compounds were reported. Finally, the intra molecular hydrogen bonding interaction between oxygen and hydrogen atoms within the same compound was discussed .It was shown that the compound with the NO_2 substituent has the stronger intra hydrogen bonding interaction.

الخلاصة

استعملت طريقة الحساب PM3 التقريبية شبة التجريبية المحملة في برنامج كاوس -03 لأيجاد الشكل الهندسي المستقر و عزم ثنائي القطب و الكثافات الألكترونية و طاقة اعلى مدار ممتلئ و طاقة اوطأ مدار فارغ و كذلك المعطيات الثرموداينمكية U^o, H^o, S^o, G^o, و A^o لأثنى عشر من المركبات الجديدة الحاوية على حلقتي 1,3,4 الأوكسازول و 1,3,4 الثاياديازول في نفس المركب. واخيرا تمت دراسة الأصرة الهيدروجينيـة ضـمن المركب الواحد . وتبين ان مثل هذه الأصرة في المركب المتضمن مجموعة NO_2 تمثل أقوى الأواصر مقارنـة بمثيلاتها في باقي المركبات في هذه الدراسة.

Introduction

The efficient of heterocyclic unit on liquid crystalline behavior was investigated[1].and the synthesis of some of mesogenic heterocyclic compounds was carried out[2-4]. The influence of 1,3,4-oxadiazole and 1,3,4-thiadiazole unit on mesomorphic behavior have been reported[5-8].Recently some symmetrical bi-1,3,4-oxadiazole derivatives were synthesized[9,10].Later, a novel thermotropic liquid crystalline

compounds containing two types of heterocyclic ring in the same molecule namely, 1,3,4-oxadiazole and 1,3,4-thiadiazole rings with SCH_2 bridge were , also, prepared. These compounds have the following formula

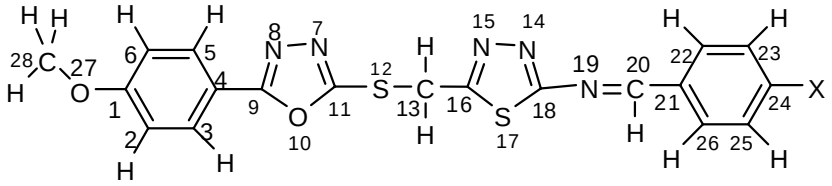


Fig.1-a

where X is H , the unsubstituted compound, NO_2 , Cl , OCH_3, OC_2H_5 , OC_3H_7 , OC_4H_9 , OC_5H_{11}, OC_6H_{13} , OC_7H_{15} , OC_8H_{17} , $-OCOCH_3$, $-OCOC_7H_{15}$ substituents , Fig. 1. The indicated atoms have the same numbers in all of these compounds.

In this work the PM3 semi empirical MO[12] method within the Gaussian03 software package on a personal computer[12] was applied to calculate the optimized geometries of these compounds along with the calculation of some of their physical properties.

Structural Details

The substitution of hydrogen attached to C_{24} atom, in the parent compound , Fig.1-a, by the X group , leads to increase the adjacent bonds length (Table1) . This effect is more pronounced for substituents with the strong electron donating behavior, OR, where R is CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}. C_7H_{15}, C_8H_{17}, and less effect is shown by moderately donating groups, -OCOR, where R is CH_3 and C_7H_{15}. All the substituents are found to produce a small increase in bond angle to which the substituent is attached, with the exception of the NO_2 substituent .The higher increment of bond angle is shown for compound of the $-OCOCH_3$ group. This may be due to the repulsion between the electron pairs on two oxygen atoms which leads to open the apex angle to a large extent In contrast , the compound with NO_2 has the smallest angle due to its higher dipole moment.

Dipole Moments

The compounds with the NO_2. Cl , $-OCOCH_3$ and $-OCOC_7H_{15}$ substituents have dipole moments higher than that in the case of the unsubstituted compound while the dipole moments of the compounds of the remaining substituents are less than that of the parent one, Table 2.

Orbital Energies

According to Koopman s' theorem (the negative HOMO energy is equal to the ionization energy).The NO_2, $-OCOCH_3$, $-OCOC_7H_8$, and Cl substituents are found to decrease the energy of HOMO and LUMO (Table-2) to a certain degree .This effect is more pronounced in the case of NO_2 substituent. The low energy of LUMO suggests a high reactivity (Table-2).The OCH_3, OC_2H_5, OC_3H_7, OC_4H_9, OC_5H_{11}, OC_6H_{13}, OC_7H_{15}, OC_8H_{17} substituents increase the energy of LUMO .The most effect is shown with OC4H9 group. Also, the increment in case of $-OCOCH_3$ is more than that in case of $-OCOC_7H_{15}$.This is may be due to the

hyper conjunction effect. The high energy of LUMO suggests a high stability.

Electron Densities

The NO_2 and the Cl groups increase the negative charge at the C atom to which the subsitiuent is attached compared with that at the two adjacent C atoms. In case of compounds with the OCH_3, $-OCOCH_3$ and $-OCOC_7H_{15}$ substituents , the C atom attached to the group have positive charge , Table 3.

Thermodynamics Data

From Table 4, the entropy, S^o for the substituted compounds is higher than that of the unsubstituted compound, (i.e compound 1).In addition to, S^o is increased as the atoms of the substituent is increased The same thing is shown for the H^o and U^o thermodynamics functions except that with the case of the Cl substituent.

Intramolecular Hydrogen Bonding Interaction

One type of intra molecular hydrogen bonding interaction between the oxygen atom, O_{27}, see Fig. 1-b , in the methoxy group, and one hydrogen of the same group, is showing in all of these of compounds and also for the unsubstituted compound, mentioned before. A second type of intra molecular hydrogen bonding interaction between the oxygen atom, O_{29} , and the one hydrogen of the adjacent methylene group was also shown for some of these compound , Table 5. The intra molecular distances of the oxygen and hydrogen atom , for these two types were reported in Table 5. It is obvious that the intramolecular hydrogen bonding of the first type is the stronger one due to its shorter distance between O_{27} and the hydrogen atom .Also, The compound with NO_2 substituent shows the shorter intra molecular hydrogen distance. This may be due to high dipole moment of this substituent , Table 2.

Table -1: Comparison of selected geometric parameters for the studied compounds. Bond lengths, R, in angstrom and bond angles , A, in degree: See Fig.1

Bond length(bond angle)	H	NO_2	Cl	OCH_3	OC_2H_5	OC_3H_7
R(1-2)	1.4062	1.4064	1.4063	1.4062	1.4062	1.4062
R(1-6)	1.3990	1.3991	1.3991	1.3990	1.3910	1.3990
R(1-27)	1.3764	1.3761	1.3764	1.3764	1.3764	1.3765
R(2-3)	1.3842	1.3841	1.3842	1.3842	1.3842	1.3843
R(3-4)	1.4023	1.4024	1.4023	1.4023	1.4023	1.4023
R(4-5)	1.3985	1.3986	1.3985	1.3985	1.3985	1.3985
R(4-9)	1.4524	1.4522	1.4523	1.4524	1.4524	1.4524
R(5-6)	1.3893	1.3892	1.3893	1.3893	1.3893	1.3893
R(7-8)	1.3505	1.3505	1.3506	1.3505	1.3505	1.3505
R(7-11)	1.3376	1.3375	1.3375	1.3375	1.3375	1.3375
R(8-9)	1.3371	1.3371	1.3371	1.3371	1.3371	1.3371
R(9-10)	1.3793	1.3795	1.3794	1.3792	1.3793	1.3793
R(10-11)	1.3802	1.3800	1.3802	1.3803	1.3802	1.3802
R(11-12)	1.7520	1.7522	1.7520	1.7520	1.7520	1.7520
R(12-13)	1.8303	1.8294	1.8301	1.8304	1.8304	1.8304

R(13-16)	1.4812	1.4818	1.4813	1.4812	1.4811	1.4811
R(14-15)	1.3349	1.3329	1.3347	1.3351	1.3351	1.3351
R(14-18)	1.3507	1.3511	1.3508	1.3510	1.3510	1.3510
R(15-16)	1.3419	1.3439	1.3421	1.3418	1.3418	1.3418
R(16-17)	1.7649	1.7625	1.7647	1.7647	1.7647	1.7649
R(17-18)	1.7664	1.7626	1.7657	1.7670	1.7671	1.7671
R(18-19)	1.4083	1.4109	1.4085	1.4072	1.4071	1.4071
R(19-20)	1.2870	1.2868	1.2869	1.2876	1.2876	1.2875
R(20-21)	1.4705	1.4732	1.4708	1.4686	1.4683	1.4685
R(21-22)	1.3965	1.3953	1.3970	1.3988	1.3991	1.3987
R(21-26)	1.3948	1.3942	1.3955	1.3948	1.3943	1.3948
R(22-23)	1.3895	1.3887	1.3887	1.3859	1.3852	1.3859
R(23-24)	1.3918	1.3999	1.3937	1.4040	1.4059	1.4044
R(24-25)	1.3906	1.3992	1.3926	1.3990	1.3992	1.3993
R(24-29)*	1.0951	1.4997	1.6835	1.3794	1.3744	1.3787
R(25-26)	1.3914	1.3902	1.3905	1.3890	1.3892	1.3888
R(27-28)	1.4071	1.4072	1.4072	1.4071	1.4071	1.4071
A(2-1-6)	120.5	120.5	120.5	120.5	120.5	120.5
A(2-1-27)	114.0	114.0	114.0	114.0	114.0	114.0
A(1-2-3)	119.5	119.5	119.5	119.5	119.5	119.5
A(6-1-27)	125.5	125.5	125.5	125.5	125.5	125.5
A(1-6-5)	119.5	119.5	119.5	119.5	119.5	119.5
A(1-27-28)	117.7	117.7	117.7	117.7	117.7	117.7
A(2-3-4)	120.3	120.3	120.3	120.3	120.3	120.3
A(3-4-5)	119.9	119.9	119.9	119.9	119.9	119.9
A(3-4-9)	121.1	121.1	121.1	121.1	121.1	121.1
A(5-4-9)	119.1	119.1	119.1	119.1	119.1	119.1
A(4-5-6)	120.4	120.3	120.4	120.4	120.4	120.4
A(4-9-8)	130.8	130.8	130.8	130.8	130.8	130.8
A(4-9-10)	121.3	121.3	121.3	121.3	121.3	121.3
A(8-7-11)	109.3	109.2	109.3	109.3	109.3	109.3
A(7-8-9)	108.6	108.6	108.6	108.6	108.6	108.6
A(7-11-10)	107.4	107.4	107.4	107.4	107.4	107.4
A(7-11-12)	131.7	131.7	131.7	131.7	131.7	131.8
A(8-9-10)	107.9	107.9	107.9	107.9	107.9	107.9
A(9-10-11)	106.9	106.9	106.9	106.9	106.9	106.9
A(10-11-12)	120.9	120.9	120.9	120.8	120.8	120.8
A(11-12-13)	103.6	103.5	103.6	103.6	103.6	103.6
A(12-13-16)	114.0	114.0	114.0	114.0	114.0	114.0
A(13-16-15)	121.6	121.4	121.6	121.6	121.6	121.6
A(13-16-17)	125.1	125.2	125.1	125.1	125.1	125.1
A(15-14-18)	113.0	113.0	113.0	113.0	113.0	113.0
A(14-15-16)	114.1	114.0	114.1	114.1	114.1	114.1
A(14-18-17)	113.5	113.5	113.5	113.4	113.4	113.4
A(14-18-19)	121.7	122.2	121.7	121.8	121.8	121.8

A(15-16-17)	113.3	113.3	113.3	113.3	113.3	113.3
A(16-17-18)	86.1	86.1	86.1	86.1	86.1	86.1
A(17-18-19)	124.4	123.9	124.4	124.3	124.3	124.3
A(18-19-20)	128.5	127.9	128.5	128.8.	128.8	128.8
A(19-20-21)	128.3	128.0	128.3	128.6	128.6	128.6
A(20-21-22)	118.8	119.7	118.7	118.6	118.5	118.4
A(20-21-26)	121.0	120.0	120.9	121.3	121.4	121.3
A(22-21-26)	120.2	120.3	120.4	120.2	120.1	120.2
A(21-22-23)	119.8	120.0	119.9	120.4	120.4	120.4
A(21-26-25)	119.6	119.9	119.8	120.0	120.1	120.0
A(22-23-24)	120.1	119.9	119.4	119.1	119.2	119.1
A(23-24-25)	120.1	119.9	120.9	120.7	120.5	120.6
A(23-24-29)*	119.9	120.0	119.5	114.9	114.3	114.8
A(25-24-29)*	120.0	120.1	119.6	124.3	125.2	124.5
A(24-25-26)	120.3	120.0	119.6	119.6	119.7	119.6

Table 1:contd.

Bond length(bond angle)	OC_4H_9	OC_5H_{11}	OC_6H_{13}	OC_7H_{15}	OC_8H_{17}	$OCOCH_3$	$OCOC_7H_{15}$
R(1-2)	1.4062	1.4062	1.4062	1.4062	1.4062	1.4063	1.4063
R(1-6)	1.3990	1.3990	1.3990	1.3990	1.3990	1.3991	1.39991
R(1-27)	1.3765	1.3765	1.3765	1.3765	1.3843	1.3763	1.3762
R(2-3)	1.3843	1.3843	1.3843	1.3843	1.3843	1.3842	1.3842
R(3-4)	1.4023	1.4023	1.4023	1.4023	1.4023	1.4023	1.4024
R(4-5)	1.3985	1.3985	1.3985	1.3985	1.3985	1.3985	1.3986
R(4-9)	1.4524	1.4524	1.4524	1.4524	1.4524	1.4523	1.4523
R(5-6)	1.3893	1.3893	1.3893	1.3893	1.3893	1.3893	1.3893
R(7-8)	1.3505	1.3505	1.3505	1.3505	1.3505	1.3506	1.3505
R(7-11)	1.3375	1.3375	1.3375	1.3375	1.3375	1.3375	1.3375
R(8-9)	1.3371	1.3371	1.3371	1.3371	1.3371	1.3370	1.3372
R(9-10)	1.3793	1.3793	1.3793	1.3793	1.3793	1.3795	1.3794
R(10-11)	1.3802	1.3802	1.3802	1.3802	1.3802	1.3801	1.3801
R(11-12)	1.7520	1.7520	1.7520	1.7520	1.7520	1.7520	1.7522
R(12-13)	1.8304	1.8304	1.8304	1.8304	1.8304	1.8299	1.8300
R(13-16)	1.4811	1.4811	1.4811	1.4811	1.4811	1.4814	1.4815
R(14-15)	1.3351	1.3351	1.3351	1.3351	1.3351	1.3346	1.3342
R(14-18)	1.3510	1.3510	1.3510	1.3510	1.3510	1.3509	1.3509
R(15-16)	1.3418	1.3418	1.3418	1.3418	1.3418	1.3422	1.3430
R(16-17)	1.7648	1.7648	1.7648	1.7648	1.7648	1.7646	1.7632
R(17-18)	1.7670	1.7670	1.7670	1.7670	1.7670	1.7650	1.7651
R(18-19)	1.4071	1.4072	1.4072	1.4072	1.4072	1.4085	1.4096
R(19-20)	1.2875	1.2875	1.2875	1.2875	1.2875	1.2867	1.2875
R(20-21)	1.4685	1.4685	1.4685	1.4685	1.4685	1.4707	1.4714
R(21-22)	1.3987	1.3987	1.3987	1.3987	1.3980	1.3970	1.3959
R(21-26)	1.3948	1.3948	1.3948	1.3948	1.3948	1.3956	1.3950

R(22-23)	1.3859	1.3859	1.3859	1.3859	1.3859	1.3887	1.3885
R(23-24)	1.4044	1.4044	1.4044	1.4044	1.4044	1.3996	1.4014
R(24-25)	1.3993	1.3993	1.3993	1.3993	1.3993	1.3988	1.3991
R(24-29)	1.3787	1.3787	1.3787	1.3787	1.3787	1.3908	1.3851
R(25-26)	1.3888	1.3888	1.3888	1.3888	1.3888	1.3902	1.3891
R(27-28)	1.4071	1.4071	1.4071	1.4071	1.4071	1.4072	1.4072
A(2-1-6)	120.5	120.5	120.5	120.5	120.5	120.5	120.5
A(2-1-27)	114.0	114.0	114.0	114.0	114.0	114.0	114.0
A(1-2-3)	119.5	119.5	119.5	119.5	119.5	119.5	119.5
A(6-1-27)	125.5	125.5	125.5	125.5	125.5	125.5	125.5
A(1-6-5)	119.5	119.5	119.5	119.5	119.5	119.5	119.5
A(1-27-28)	117.7	117.7	117.7	117.7	117.7	117.7	117.7
A(2-3-4)	120.3	120.3	120.3	120.3	120.3	120.3	120.3
A(3-4-5)	119.9	119.9	119.9	119.9	119.9	119.9	119.9
A(3-4-9)	121.1	121.1	121.1	121.1	121.1	121.1	121.1
A(5-4-9)	119.1	119.1	119.1	119.1	119.1	119.1	119.1
A(4-5-6)	120.4	120.4	120.4	120.4	120.4	120.4	120.4
A(4-9-8)	130.8	130.8	130.8	130.8	130.8	130.8	130.8
A(4-9-10)	121.3	121.3	121.8	121.3	121.3	121.3	121.3
A(8-7-11)	109.3	109.3	109.3	109.3	109.3	109.2	109.2
A(7-8-9)	108.6	108.6	108.6	108.6	108.6	108.6	108.6
A(7-11-10)	107.4	107.4	107.4	107.4	107.4	107.4	107.4
A(7-11-12)	131.8	131.8	131.8	131.8	131.8	131.7	131.7
A(8-9-10)	107.9	107.9	107.9	107.9	107.9	107.9	107.9
A(9-10-11)	106.9	106.9	106.9	106.9	106.9	106.9	106.9
A(10-11-12)	120.8	120.8	120.8	120.8	120.8	120.9	120.9
A(11-12-13)	103.6	103.6	103.6	103.6	103.6	103.6	103.5
A(12-13-16)	114.0	114.0	114.0	114.0	114.0	114.1	114.0
A(13-16-15)	121.6	121.6	121.6	121.6	121.6	121.6	121.5
A(13-16-17)	125.1	125.1	125.1	125.1	125.1	125.1	125.2
A(15-14-18)	113.0	113.0	113.0	113.0	113.0	113.0	113.0
A(14-15-16)	114.1	114.1	114.1	114.1	114.1	114.1	114.0
A(14-18-17)	113.4	113.4	113.4	113.4	113.4	113.5	113.5
A(14-18-19)	121.8	121.8	121.8	121.8	121.8	121.6	122.2
A(15-16-17)	113.3	113.3	113.3	113.3	113.3	113.3	113.3
A(16-17-18)	86.1	86.1	86.1	86.12	86.1	86.1	86.1
A(17-18-19)	124.3	124.3	124.3	124.3	124.3	124.4	123.9
A(18-19-20)	128.8	128.8	128.8	128.8	128.8	128.7	127.9
A(19-20-21)	128.6	128.6	128.6	128.6	128.6	128.5	127.9
A(20-21-22)	118.4	118.4	118.4	118.4	118.4	118.5	119.5
A(20-21-26)	121.3	121.3	121.3	121.3	121.3	121.1	120.0
A(22-21-26)	120.2	120.2	120.3	120.2	120.2	120.4	120.5
A(21-22-23)	120.4	120.4	120.4	120.4	120.4	120.2	120.1
A(21-26-25)	120.0	120.0	1230.0	120.0	120.0	120.0	119.9
A(22-23-24)	119.1	119.1	119.1	119.1	110.1	119.0	119.2

A(23-24-25)	120.6	120.6	120.6	120.6	120.6	121.2	120.8
A(23-24-29)	114.8	114.8	114.8	114.8	114.8	117.9	123.2
A(25-24-29)	124.5	124.5	124.5	124.5	124.5	120.7	123.2
A(24-25-26)	119.6	119.6	119.6	119.6	119.6	119.2	119.4

* For unsubstituted compound, atom number ,29, is replaced by atom number,38. .

Table 2. Calculated total energy (in a.u) , dipole moments (Debye) ,orbital energies(HOMO, LUOMO, a.u) , the difference between energy of HOMO and LUMO (Δ,a.u) and ionization energies (IP, a.u) for the studied compounds. See Fig 1.

Substituent, X	Total energy, a.u	Dipole moment , μ	E_{HOMO}, a.u	E_{LUMO}, a.u	$\Delta(E_{HOMO}-E_{LUMO})$, a.u	IP , a.u
H	0.20936420	2.6075	-0.32841	-0.05497	0.27344	0.32841
NO_2	0.19747745	6.7970	-0.33253	-0.06814	0.26439	0.33253
Cl	0.19906414	2.8222	-0.32913	-0.05725	0.27188	0.32913
OCH_3	0.14821549	1.5360	-0.32826	-0.05455	0.27371	0.32826
OC_2H_5	0.14035289	1.5228	-0.32807	-0.05409	0.27398	0.32807
OC_3H_7	0.13007073	1.5796	-0.32794	-0.05389	0.27405	0.32794
OC_4H_9	0.12145976	1.5825	-0.32795	-0.05388	0.27406	0.32795
OC_5H_{11}	0.11279511	1.5761	-0.32794	-0.05389	0.27405	0.32794
OC_6H_{13}	0.10414104	1.5681	-0.32795	-0.05390	0.27405	0.32795
OC_7H_{15}	0.09547836	1.5681	-0.32794	-0.05391	0.27403	0.32794
OC_8H_{17}	0.08681581	1.5696	-0.32795	-0.05392	0.27403	0.32795
$OCOCH_3$	0.07982240	4.9410	-0.32969	-0.05917	0.27052	0.32969
$OCOC_7H_{15}$	0.03060723	4.1632	-0.33096	-0.06163	0.26933	0.33096

Table-3: The Charge electron densities for the atoms of the studied compounds. See Fig 1.

Atom no.	H	NO_2	Cl	OCH_3	OC_2H_5	OC_3H_7	OC_4H_9
1	0.118	0.120	-0.119	0.118	0.118	0.118	0.118
2	-0.151	-0.150	-0.151	-0.151	-0.151	-0.151	-0.151
3	-0.031	-0.030	-0.031	-0.031	-0.031	-0.031	-0.031
4	-0.085	-0.087	-0.085	-0.085	-0.085	-0.085	-0.085
5	-0.010	-0.009	-0.010	-0.010	-0.010	-0.010	-0.010
6	-0.196	-0.196	-0.196	-0.196	-0.196	-0.196	-0.196
7	-0.102	-0.103	-0.102	-0.102	-0.102	-0.102	-0.102
8	-0.094	-0.094	-0.094	-0.094	-0.094	-0.094	-0.094
9	0.053	0.056	-0.054	0.053	-0.053	0.053	0.053
10	-0.073	-0.072	-0.073	-0.073	-0.073	-0.073	-0.073
11	-0.150	-0.153	-0.151	-0.150	-0.150	-0.150	-0.150
12	0.194	0.200	0.195	0.193	0.193	0.193	0.193
13	-0.831	-0.088	-0.084	-0.083	-0.082	-0.082	-0.082

14	-0.091	-0.080	-0.091	-0.097	-0.097	-0.097	-09.097
15	0.006	0.002	0.006	0.006	0.006	0.006	0.006
16	-0.289	-0.280	-0.287	-0.291	-0.291	-0.291	-0.291
17	0.331	0.357	0.335	0.330	0.329	0.329	0.329
18	-0.185	-0.211	-0.189	-0.179	-0.178	-0.179	-0.179
19	-0.024	-0.011	-0.021	-0.030	-0.031	-0.030	-0.030
20	0.047	0.021	0.043	0.056	0.058	0.056	0.056
21	-0.131	-0.057	-0.132	-0.174	-0.178	-0.175	-0.175
22	-0.076	-0.105	-0.063	-0.040	-0.037	-0.039	-0.039
23	-0.105	-0.010	-0.108	-0.145	-0.150	-0.147	-0.147
24	-0.084	-0.397	-0.113	0.107	0.117	0.109	0.109
25	-0.102	-0.005	-0.104	-0.190	-0.196	-0.192	-0.191
26	-0.059	-0.079	-0.046	-0.017	-0.015	-0.018	-0.018
27	-0.184	-0.184	-0.184	-0.184	-0.184	-0.184	-0.184
28	0.050	0.500	0.050	0.050	-0.050	0.050	0.050
29	0.126	1.305	0.077	-0.188	-0.189	-0.186	-0.186
30	0.116	-0.594	0.126	0.045	-0.124	-0.105	-0.110
31	0.126	-0.597	0.115	0.126	0.050	-0.134	-0.091
32	0.122	0.127	0.126	0.116	0.126	0.044	0.141
33	0.118	0.115	0.122	0.126.	0.116	0.126	0.045
34	0.114	0.126	0.119	0.122	0.126	0.116	0.126
35	0.113	0.123	0.114	0.118	0.122	0.126	0.116
36	0.108	0.120	0.115	0.114	0.118	0.122	0.126
37	0.108	0.115	0.110	0.112	0.114	0.118	0.122
38	0.105	0.119	0.121	0.106	0.111	0.114	0.118
39	0.110	0.136	0.123	0.125	0.106	0.111	0.114
40	0.125	0.137	0.128	0.126	0.125	0.106	0.111
41	0.054	0.128	0.053	0.126	0.126	0.125	0.106
42	0.031	0.054	0.031	0.054	0.126	0.127	0.125
43	0.031	0.031	0.031	0.031	0.054	0.127	0.127
44		0.031		0.031	0.031	0.054	0.127
45				0.052	0.031	0.031	0.054
46				0.030	0.048	0.031	0.031
47				0.036	0.053	0.043	0.031
48					0.050	0.038	0.040
49					0.042	0.040	0.040
50					0.047	0.064	0.064
51						0.059	0.059
52						0.064	0.064
53						0.051	0.051

Table 3:contd.

Atom no.	OC_5H_{11}	OC_6H_{13}	OC_7H_{15}	OC_8H_{17}	$OCOCH_3$	$OCOC_7H_{15}$
1	0.118	0.118	0.118	0.118	0.119	0.119
2	-0.151	-0.151	-0.151	-0.150	-0.151	-0.151
3	-0.031	-0.031	-0.031	-0.031	-0.031	-0.030
4	-0.085	-0.085	-0.085	-0.085	-0.086	-0.086
5	-0.010	-0.010	-0.010	-0.010	-0.010	-0.009
6	-0.196	-0.196	-0.196	-0.196	0.196	-0.196
7	-0.102	-0.102	-0.102	-0.102	-0.103	-0.102
8	-0.094	-0.094	-0.094	-0.094	-0.094	-0.094
9	-0.053	0.053	0.053	0.053	0.054	0.055
10	-0.073	-0.073	-0.073	-0.073	-0.073	-0.073
11	-0.150	-0.150	-0.150	-0.150	-0.151	-0.152
12	-0.193	0.193	0.193	0.193	0.196	0.196
13	-0.082	-0.082	-0.082	-0.082	-0.085	-0.085
14	-0.097	-0.097	-0.097	-0.097	-0.092	-0.089
15	0.006	0.006	0.006	0.006	0.006	0.000
16	-0.291	-0.291	-0.291	-0.291	-0.285	-0.286
17	0.329	0.329	0.329	0.329	0.340	0.343
18	-0.179	-0.179	-0.179	-0.179	-0.192	-0.191
19	-0.030	-0.030	-0.030	-0.030	-0.174	-0.027
20	0.056	0.056	0.056	0.056	0.039	0.048
21	-0.175	-0.175	-0.175	-0.175	-0.136	-0.143
22	-0.039	-0.039	-0.039	-0.039	-0.060	-0.056
23	-0.147	-0.147	-0.147	-0.147	-0.117	-0.118
24	0.109	0.109	0.109	0.109	0.061	0.075
25	-0.191	-0.191	-0.191	-0.191	-0.130	-0.157
26	-0.018	-0.018	-0.018	-0.018	-0.044	-0.027
27	-0.184	-0.184	-0.184	-0.184	-0.184	-0.183
28	0.050	0.050	0.050	0.050	0.050	0.050
29	-0.186	-0.186	-0.186	-0.186	-0.190	-0.192
30	-0.110	-0.109	-0.109	-0.109	0.356	0.353
31	-0.097	-0.097	-0.097	-0.097	-0.323	-0.319
32	-0.097	-0.103	-0.103	-0.103	-0.139	-0.109
33	-0.139	-0.096	-0.102	-0.102	0.126	-0.097
34	0.045	-0.139	-0.096	-0.102	0.115	-0.103
35	0.126	0.045	-0.140	-0.096	0.126	-0.099
36	0.116	0.126	0.045	-0.140	0.123	-0.108
37	0.126	0.116	0.126	0.045	0.119	-0.091
38	0.122	0.126	0.116	0.126	0.115	-0.125
39	0.118	0.122	0.126	0.116	0.114	0.126
40	0.114	0.118	0.122	0.126	0.111	0.115
41	0.111	0.114	0.118	0.122	0.125	0.126
42	0.106	0.111	0.114	0.118	0.124	0.123

43	0.125	0.106	0.111	0.114	0.131	0.118
44	0.127	0.125	0.106	0.111	0.054	0.115
45	0.054	0.127	0.125	0.106	0.031	0.116
46	0.031	0.127	0.127	0.125	0.031	0.110
47	0.031	0.054	0.127	0.127	0.079	0.127
48	0.031	0.031	0.054	0.127	0.072	0.123
49	0.039	0.031	0.031	0.054	0.072	0.120
50	0.038	0.038	0.031	0.031		0.054
51	0.050	0.038	0.038	0.031		0.031
52	0.050	0.038	0.038	0.037		0.031
53	0.050	0.049	0.038	0.038		0.037
54	0.052	0.049	0.049	0.038		0.039
55	0.066	0.053	0.049	0.048		0.037
56	0.061	0.052	0.051	0.049		0.048
57	0.064	0.050	0.051	0.051		0.050
58	0.051	0.052	0.052	0.051		0.054
59		0.067	0.052	0.051		0.050
60		0.061	0.051	0.051		0.050
61		0.051	0.052	0.052		0.055
62		0.064	0.067	0.053		0.065
63			0.061	0.052		0.048
64			0.064	0.051		0.056
65			0.051	0.061		0.071
66				0.067		0.080
67				0.051		0.087
68				0.064		

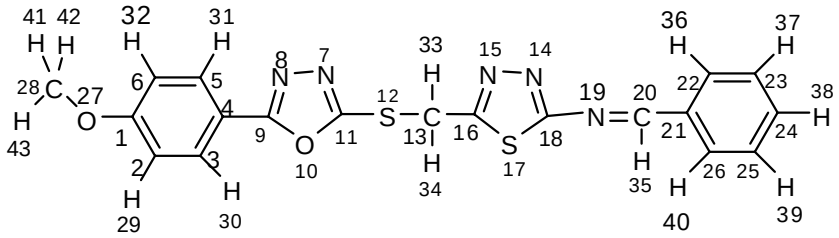
Table 4*. Thermodynamic data of the studied compounds at 25° C.

substituent	U^o	H^o	S^o	G^o	A^o	E_0	C_v
H	211.282	213.760	192.697	156.307	153.829	195.444	92.623
NO_2	215.341	217.820	209.506	155.356	152.877	197.856	100.495
Cl	206.290	208.769	199.560	149.270	146.791	189.702	96.234
OCH_3	333.078	335.557	205.281	274.353	271.874	215.591	101.686
OC_2H_5	251.626	254.105	214.730	190.089	187.604	233.191	106.641
OC_3H_7	269.938	272.417	221.314	206.432	203.953	250.778	111.301
OC_4H_9	288.284	290.763	229.260	222.409	219.930	268.272	116.158
OC_5H_{11}	306.627	309.106	237.171	238.394	235.915	285.756	121.024
OC_6H_{13}	324.972	327.451	245.132	254.365	251.886	303.239	125.889
OC_7H_{15}	343.319	345.798	252.794	270.428	267.949	320.723	130,753
OC_8H_{17}	361.666	364.145	260.273	286.545	284.066	338.209	135.617
$OCOCH_3$	240.603	243.082	218.720	177.871	175.392	221.769	108.347
$OCOC_7H_{15}$	350.293	352.772	254.897	276.775	274.296	327.099	135.159

* U^o ; H^o; G^o; A^o , $kcal.mol^{-1}$; S^o and C_v, $cal.mol^{-1}.K^{-1}$

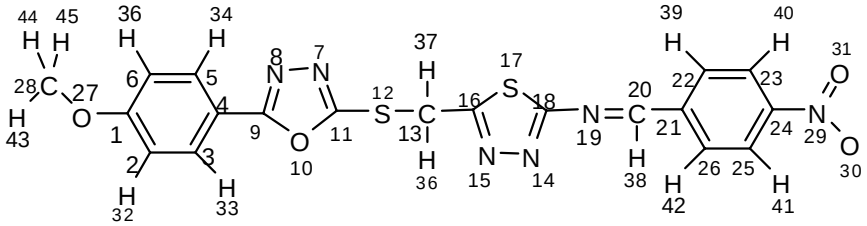
Table 5:The intra molecular hydrogen bonding distance, in Angstrom ,A^o. See Fig 1.

Substituent	O_{27}----H(CH_3)	O_{29}---H(CH_2)
H	1.95550	----------
NO_2	1.95547	-------
Cl	1.95550	-------
OCH_3	1.95550	1.96873
OC_2H_5	1.95551	--------
OC_3H_7	1.95551	1.96321
OC_4H_9	1.95551	1.96194
OC_5H_{11}	1.95551	1.96199
OC_6H_{13}	1.95551	1.96197
OC_7H_{15}	1.95551	1.96198
OC_8H_{17}	1.95551	1.96198
$OCOCH_3$	1.95549	--------
$OCOC_7H_{15}$	1.95548	-------



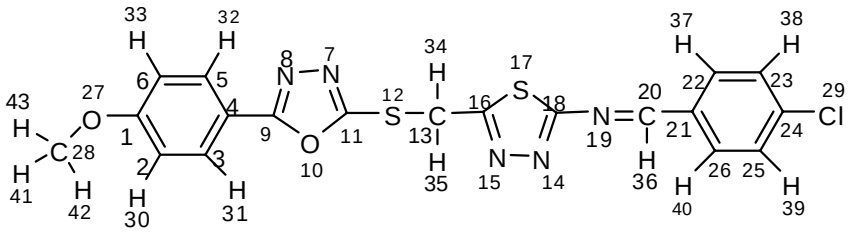
-1- (unsubstituted compound)

N-benzylidene-5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-1,3,4-thiadiazol-2-amine



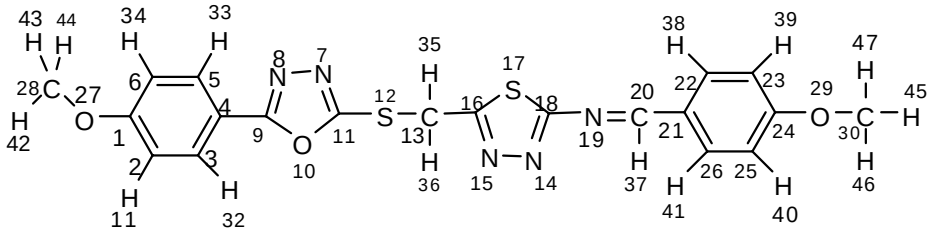
-2-

5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-*N*-(4-nitrobenzylidene)-1,3,4-thiadiazol-2-amine



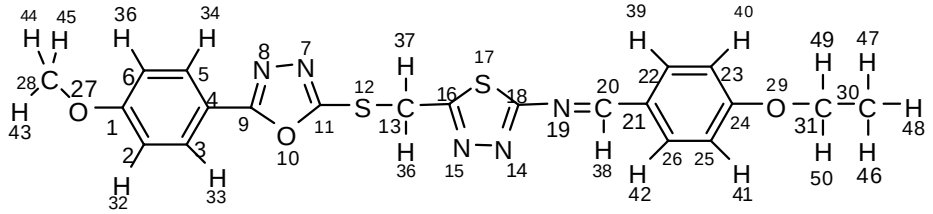
-3-

N-(4-chlorobenzylidene)-5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-1,3,4-thiadiazol-2-amine



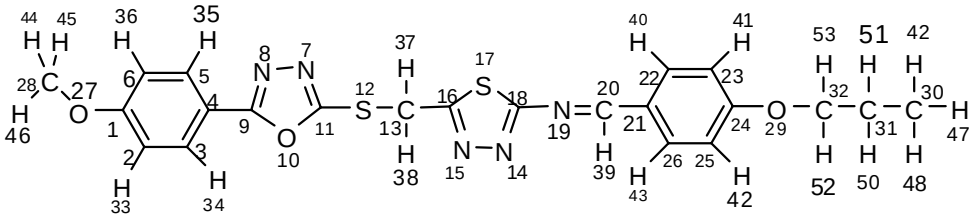
-4-

N-(4-methoxybenzylidene)-5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-1,3,4-thiadiazol-2-amine



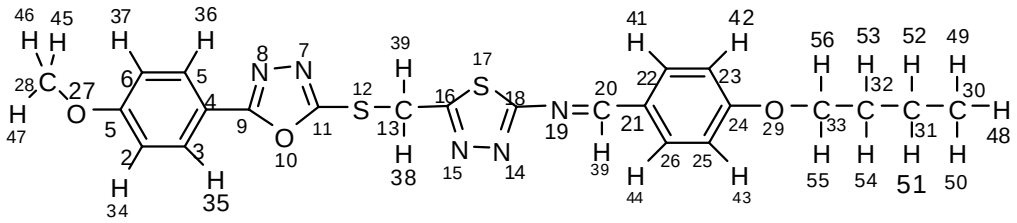
-5-

N-(4-ethoxybenzylidene)-5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-1,3,4-thiadiazol-2-amine



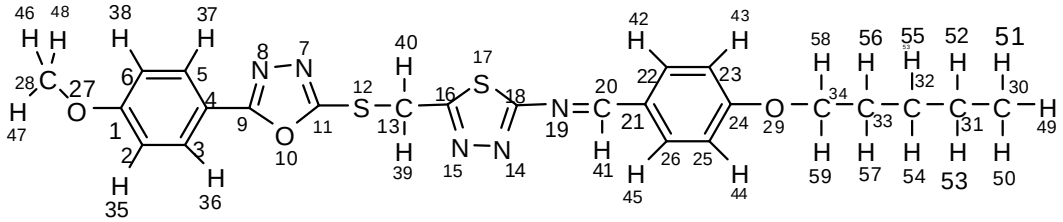
-6-

5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-*N*-(4-propoxybenzylidene)-1,3,4-thiadiazol-2-amine



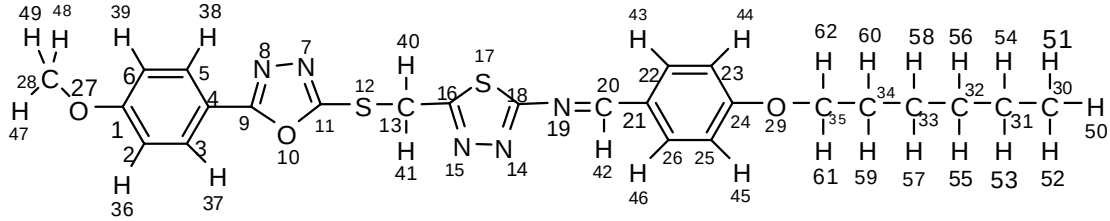
-7-

N-(4-butoxybenzylidene)-5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-1,3,4-thiadiazol-2-amine



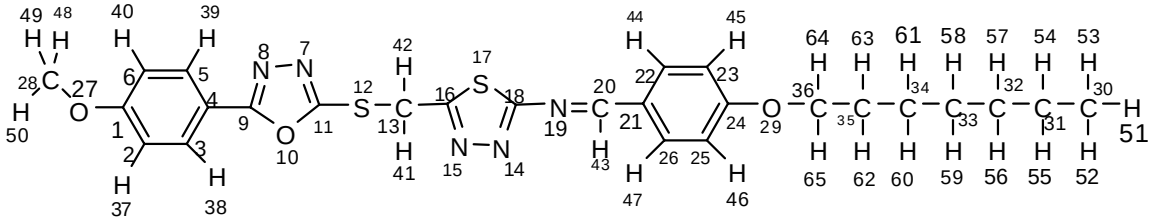
-8-

5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-*N*-(4-(pentyloxy)benzylidene)-1,3,4-thiadiazol-2-amine



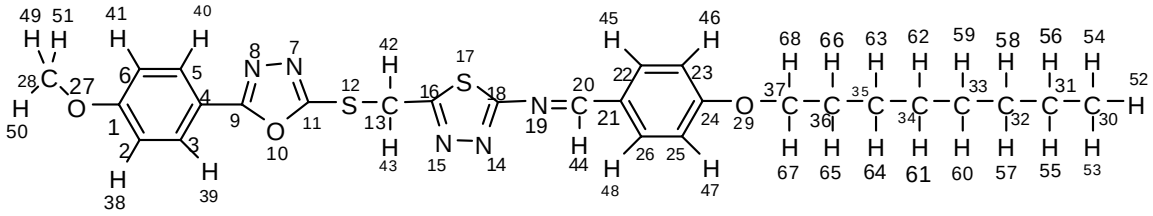
-9-

N-(4-(hexyloxy)benzylidene)-5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-1,3,4-thiadiazol-2-amine



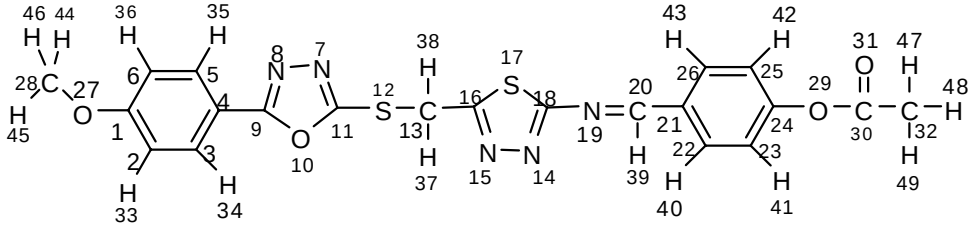
-10-

N-(4-(heptyloxy)benzylidene)-5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-1,3,4-thiadiazol-2-amine



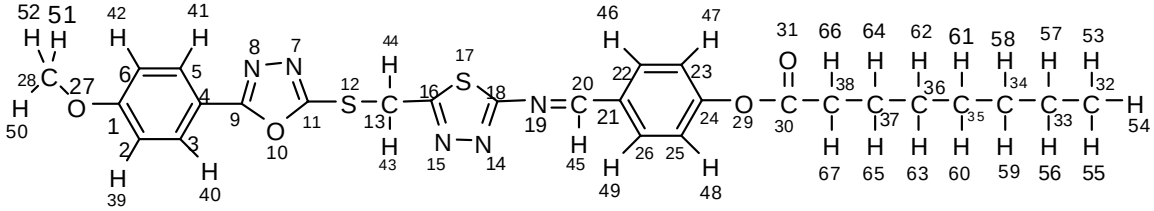
-11-

5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-*N*-(4-(octyloxy)benzylidene)-1,3,4-thiadiazol-2-amine



-12-

4-((5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-1,3,4-thiadiazol-2-ylimino)methyl)phenyl acetate



-13-

4-((5-((5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-ylthio)methyl)-1,3,4-thiadiazol-2-ylimino)methyl)phenyl octanoate

Fig.1-b. Molecular structures of the studied compounds along with atomic numbering

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