



## Stability studies of double-base propellants with centralite and malonanilide stabilizers using MO calculations in comparison to thermal studies

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### ABSTRACT

Propellants containing nitrate esters need stabilizers to avoid early decomposition or even explosion during storage. Newly prepared malonanilides **M1–M5** were tested in stabilizing double-base propellants (DBPs). Their stabilization was compared with the effect of classical stabilizer N,N'-diethyldiphenyl urea (**C1**) using both practical thermal stability tests (qualitative and quantitative tests) and theoretical molecular orbital calculations. This research shows that the new stabilizers (malonanilides) have good stabilizing effects. Some of malonanilides e.g. (**M5**) and (**M2**) have higher stability effects. Different mechanisms were suggested to explain the role of different stabilizers. Molecular orbital calculations using the semi-empirical program AM1 are performed on the new and classical stabilizers. Correlation was made between the volume (ml) of NO<sub>x</sub>, weight loss (wt%), other thermal analyses data, calculated thermodynamic parameters like activation energy ( $E_a$ , kJ mol<sup>-1</sup>) of the decomposed propellant samples containing different stabilizers and some of their calculated properties such as HOMO, LUMO energies, the charge distribution and the  $\pi$ -bond order. The stabilization effect decreases with the increase in HOMO energy. The correlation between the net charge and parameters measured for the stabilization effect shows good accordance. Comparison of the results obtained show that the high electron charge on N atom of the stabilizers and on its benzene ring is the most important factor, but not the only factor governing the stabilization effect of the stabilizers.

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### 1. Introduction

Current Navy Cartridge Actuated Devices (CADs) and Propellant Actuated Devices (PADs) use double-base propellants as either a main energetic output charge or an intermediate gas generating energetic charge. Elevated temperatures have long been known to produce degradation in both the service life and the ballistic performance and can lead to a potential cook-off safety hazard when stabilizer depletions rates are exacerbated through high temperature environmental exposure. A need exists to address these concerns and to improve double-base propellant safe life characteristics through innovations related to the long standing chemical problem of the complex reaction mechanisms known as nitrate ester degradation and its control through chemical stabilizer interaction. During storage of double-base propellants at elevated temperatures, the stabilizer reacts more and more with the nitrogen oxides (NO<sub>x</sub>) released by the nitrate esters (nitrocellulose and nitroglycerine) present in the propellant until it

has depleted completely. Although the decrease of the primary chemical stabilizer is accompanied by the additional formation of daughter stabilizer reaction products which also possess a residual stabilization capability, the depletion of the primary chemical stabilizer can lead eventually to autocatalytic decomposition of the propellant, self-heating, and cook-off. The need exists for increased propellant performance to support missions requiring high duty cycles at elevated temperatures and years of operation. The most commonly used double-base stabilizers are diphenylamine (DPA), 2-nitrodiphenylamine (2-NDPA), and ethyl centralite (EC) [1–4].

The propellant's stabilizers are substances which, by virtue of their chemical constitution, can react with the products of decomposition of smokeless powders and remove them. They do not prevent decomposition, but they stop the catalytic action of products of decomposition such as NO, NO<sub>2</sub>, HNO<sub>2</sub>, and HNO<sub>3</sub>. They stabilize the powder by removing the products of decomposition as soon as they are formed and the decomposition reaction is not catalyzed; therefore the powder will have a much longer serviceable life [5,6]. In a series of researches extending over a long period, Marquayrol [7] have determined the stabilizing effects of various substances particularly naphthalene, nitronaphthalene,

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N,N-diphenylbenzamide. Many other stabilizers have been examined by using various techniques [8–11].

The malonanilides show many applications, viz: dyes and pigments [12–14], pharmaceuticals [15], stabilizers for polymers [16–18], anti-inflammatory action [19], other industrial applications [20,21] and thermal recording materials [22]. Stabilizers must possess certain properties [5,6]. They are used in small quantities and yet impart good stability of the propellant powder. Neither the stabilizers nor their products of transformation should have any action on the powder's constituents. They should not be volatile at ambient temperatures. A good stabilizer for double-base powder (DBP) should, meanwhile, be a good gelatinizer [23]. All of these properties and activities of the stabilizers depend on their internal electronic structures. In this article the stability effects of these compounds as stabilizers for DBPs will be measured experimentally. The geometrical and structural parameters of these stabilizers are calculated and then correlated with their experimental obtained values in order to pinpoint the structural factors underlining the stabilizing activity. Therefore, this research combined both theoretical (MO) and practical techniques (TA) to evaluate the possibility of using malonanilides as DBPs stabilizers in comparison with classical stabilizer N,N'-diethyldiphenyl urea (**C1**).

## 2. Materials and methods

### 2.1. Preparation of malonoanilides

Preparation of malonanilide itself is well known in literature and it has been prepared by the method of Chattaway and Olmsted [24]. **M2** was obtained by heating ethylmalonate with N-ethylaniline till boiling for 30 min (yield 73%) and crystallized from acetic acid (m.p. 229.3 °C). Two methods were used to prepare **M3**, an old well known one in literature [26] and a new one done in our lab. In this method 5 g of malonic acid and 13 g of o-nitroaniline were added to a 500 ml round bottom flask containing 250 ml benzene. The mixture was refluxed for 6 h using Dean and Stark apparatus. The solvent was evaporated yielding **M3** product which was recrystallized from ethanol (m.p. 189 °C). Both **M4** and **M5** were prepared by the method of Walter [25] by mixing 25 ml (1.5 mol) of ethylmalonate with 27.5 g (2 mol) of m- or p-nitroaniline in 250 ml round bottom flask. The mixture was refluxed for 1 h at 200 °C.

The <sup>1</sup>H NMR spectrum of **M1** (DMSO-d<sub>6</sub>) showed peaks at δ = 3.5 ppm (s, 2H, CH<sub>2</sub>), 7.6 ppm (d, 4H, arom.), 7.3–7.0 ppm (m, 6H, arom.) and 10.1 ppm (s, 2H, NH). The <sup>1</sup>H NMR spectrum of **M2** showed peaks at δ = 1.25 ppm (t, 6H, CH<sub>3</sub>), 4.4 ppm (q, 4H, CH<sub>2</sub>), 5.6 ppm (s, 1H, CH=C), 7.6 ppm (m, 6H, arom.), 8.2 ppm (m, 4H, arom.) and 13.6 ppm (s, 1H, OH of the enolic tautomer). These data confirm the given structures in Fig. 1.

### 2.2. Preparation of the DBP samples

Samples of double-base smokeless powders were manufactured by solventless process using 3% (wt%) centralite, as a reference in sample I and 3% (wt%) of malonanilide compounds as stabilizers in samples II–VI. The used percentage of other components is given in Table 1.

Nitroglycerine, dinitrotoluene, dibutylphthalate, stabilizer and transformer oil were mixed well by gentle stirring for 2 h. The mixture was quantitatively added in small portions to the nitrocellulose continually stirred in a water medium. After the last addition, stirring was continued for 3–4 h to get the complete homogeneity of the mixture. The components were treated according to the different steps used in the production of DBP. A sample I prepared by

**Table 1**

The added components in the preparation of DBPs.

Sample	I	II	III	IV	V	VI
Stabilizer	<b>C1</b>	<b>M1</b>	<b>M2</b>	<b>M3</b>	<b>M4</b>	<b>M5</b>
Composition (wt.%)						
Nitrocellulose (12.05% N)	56	56	56	56	56	56
Nitroglycerine	27	27	27	27	27	27
Dinitrotoluene	9	9	9	9	9	9
Dibutylphthalate	4	4	4	4	4	4
Stabilizer	3	3	3	3	3	3
Transformer oil	1	1	1	1	1	1

using 3% (wt%) **C1** (centralite 1) was used as a standard sample to compare the results of the stability tests of the investigated compounds II–VI. The samples were shaped in the form of blocks and then subjected to the various stability tests.

### 2.3. Different tests used to check stability of DBPs-**M1–M5** or DBPs-**C1** mixtures

Both qualitative and quantitative tests were applied to evaluate the stability of the prepared DBPs samples containing different stabilizers (DBP-**M1–M5** or DBP-**C1**).

#### 2.3.1. Qualitative stability tests

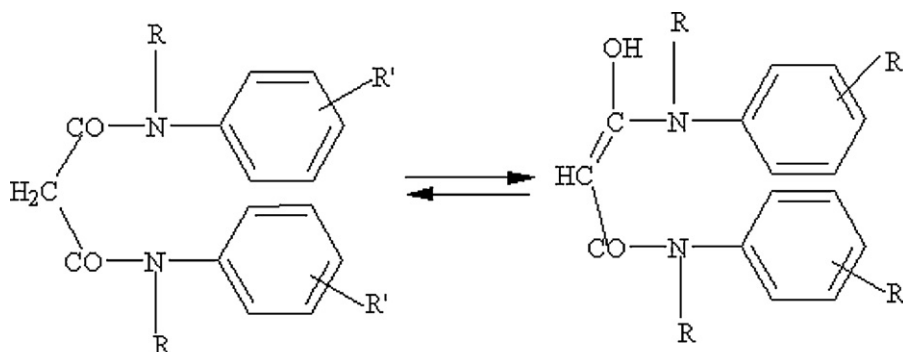
**2.3.1.1. The Abel heat test.** This test involved [26] the cut of each sample into pieces with an edge length not exceeding approximately 2 mm, and then dried at 50 °C for 16 h before carrying out the test. One gram of the prepared powder was weighed out and introduced into the test tube; the tube was closed with cork carrying the indicator paper suspended at the platinum wire. A drop of glycerol–water mixture was placed at the center of the indicator paper by means of a capillary glass dropper. The liquid drop absorbed by the indicator paper formed a circle of a diameter less than 5 mm. The test tube was immersed to a depth of approximately 7.5 cm in a heating bath which was previously maintained at 80 ± 0.5 °C. The indicator paper was watched and the time required to appear the yellow-brown circle was recorded.

**2.3.1.2. International storage test at 100 °C.** This test involved heating of a tube containing 10 ± 0.1 g samples without previous drying for 1 h at 100 °C in a heating bath (supplied by Julius Peters, Berlin). Heating was then continued after closing the tube. The upper part of the tube was examined against a white back ground every 24 h. The time in days which elapsed from the start of heating until the appearance of brown fumes was taken as a measure of the stability of the tested powder.

#### 2.3.2. Quantitative stability tests

**2.3.2.1. Stability Dutch heat test at 105 °C.** In this test the ground powder was separated on a sieve with 0.5 mm meshes in order to obtain grains smaller than 0.5 mm. Four grams of the powder were weighed out into metal tubes with a length of 160 mm, an inner diameter of 15 mm and an outer diameter of 17 mm and placed in the bath. The bath was filled with glycerol and water to about 5 cm below the upper rim and the boiling point of the liquid was regulated at 105 ± 1 °C for nitroglycerine powder. The tubes were heated open for the first 8 h and then heated closed continuously for 72 h. The tubes were weighed after 8, 24, 48 and 72 h in order to determine their weight loss.

**2.3.2.2. Bergmann–Junk test at 120 °C.** The test was done on sample pieces with a length of approximately 3–4 mm and a diameter of 2 mm and dried at 45 °C for 16 h. The prepared powder (5 g) was introduced into the test tube and treated as explained by



- M1** , 1a, R=H, R'=H  
**M2** , b, R= C<sub>2</sub>H<sub>5</sub> , R' = H  
**M3** , c, R = H , R' = o-NO<sub>2</sub>  
**M4** , d, R = H , R' = m-NO<sub>2</sub>  
**M5** , e, R = H , R' = p-NO<sub>2</sub>

Fig. 1. Structural formulae and tautomeric equilibrium of malonanilides **M1–M5**.

Bergmann–Junk [27]. The experiment was carried out twice on each sample.

2.3.2.3. *Calorimetric test.* The calorimetric test was carried out in a calorimetric bomb with a capacity of 450 cc, as explained by Hassan [28] to estimate the calorific values of the samples, after correction of the measured temperature of the sample's combustion.

#### 2.4. Determination of deflagration temperature of DBPs

One of the most important stability tests of the treated DBP samples is the determination of their deflagration temperature. The bath used for this purpose consisted of a cylindrical vessel with 11 round holes, 8 of which of 25 mm diameter for the test tubes; one hole of 20 mm diameter for standard thermometer supported with two auxiliary thermometers and the last two holes of 6 mm diameter for stirring system. The bath was placed on a tripod over burners and gradually heated with a rate of 5 °C/min. The whole system was housed in a cupboard to protect the operator. The temperatures of the three thermometers were recorded and the mean values of the measured deflagration temperatures of the samples were used to evaluate their stability.

#### 2.5. Molecular orbital calculations

Theoretical calculations were performed at the restricted Hartree-Fock level (RHF) using the semi-empirical AM1 method [29] implemented with the MOPAC6 [30] package. The structures were fully optimized without any constraints to a gradient 0.001 at the precise level. Force field calculations were used to test the nature of each structure.

### 3. Results and discussion

In this research work some prepared and structurally investigated malonanilides **M1–M5** (Fig. 1) show superior properties as stabilizers for DBPs in comparison with the classical ones [31–34]. The acidity of these molecules could favor their use as stabilizers for DBPs.

#### 3.1. Stability tests of double-base propellants containing different stabilizers

The qualitative and quantitative stability tests are used to study the effect of stabilizers on the stabilization of DBPs. The results of these tests help the evaluation of the effect of the stabilizers on thermal stability of DBPs and also in studying the observed changes of the explosive properties of the propellants. Therefore, these tests are also used to evaluate the effect of the prepared new stabilizers (**M1–M5**) in comparison with the classical one **C1**.

The results of both qualitative and quantitative stability tests of DBPs containing different stabilizers (DBP-**C1** and DBP-**M1–M5**) are shown in Table 2. The results of qualitative stability tests (Abel heat test and storage test at 100 °C) [27] applied to DBPs, containing new stabilizers (**M1–M5**), show similar behavior with that containing classical stabilizer (**C1**). The brown circle formed on the starch paper appeared after 45 min in case of Abel test and the brown fumes began to evolve after 12 days in the case of storage test at 100 °C. The quantitative stability tests are classified into two types, the first is responsible for testing the stabilization effect of the stabilizers on thermal decomposition of DBPs (Dutch heat test and Bergmann–Junk test) [27]. The second one is used for determination of Calorific value and deflagration temperature [35] and to study the effect of the stabilizers on the explosive properties of the propellants. In Dutch quantitative stability tests, the summation of weight losses (wt%) within 24–72 h are  $\Sigma = 0.41, 0.40, 0.42, 0.48, 0.41$  and  $0.43$  for DBP-**C1** and DBP-**M1–M5**, respectively. Therefore, their stability effects on DBPs can be ordered as **M1 > C1 = M4 > M2 > M5 > M3**. From these results it is clear that, no pronounced stability difference could be observed between the effects of the new stabilizers and the classical one. The value of weight loss (wt%) within the first 8 h (0.22–0.28 wt%) may refer to the autocatalytic part of nitrate ester decomposition, which is stopped by stabilizers. But in case of Bergmann–Junk test, there is a detectable difference between the effect of the new stabilizers **M1–M5** and the classical one (**C1**). This difference is measured by the volume of 0.05 M NaOH equivalent to liberated nitrogen oxide. The Bergmann–Junk test gives 4.0 ml NaOH for DBP containing **C1**, and it gives 4.3, 3.7, 2.8, 4.9 and 4.1 ml of 0.05 M NaOH in case of DBPs containing **M1, M2, M3, M4** and **M5**, respectively.

The deflagration temperature of DBP sample containing **C1** as a classical stabilizer is 175 °C. For DBP samples containing **M2, M3**

**Table 2**  
Stability tests of DBPs containing malonanilides (DBP-M1–M5) compared with that containing classical stabilizer (DBP-C1).

DBPs-stabilizer mixture	Abel heat test at 80 °C (min)	Storage test at 100 °C (days)	Dutch heat test at 105 °C after				Bergmann–Junk test at 12 °C (ml)	Calorific value (cal/g)	Deflagration temperature at (5 °C/min)
			8 h	24 h	48 h	72 h			
DBP-C1	>45	>12	0.22	0.20	0.12	0.09	4.0	776	175
			–			$\Sigma = 0.41$			
DBP-M1	>45	>12	0.25	0.17	0.13	0.10	4.3	–	–
			–			$\Sigma = 0.40$			
DBP-M2	>45	>12	0.28	0.20	0.12	0.10	3.7	762	172
			–			$\Sigma = 0.42$			
DBP-M3	>45	>12	0.26	0.22	0.16	0.10	2.8	784	172
			–			$\Sigma = 0.48$			
DBP-M4	>45	>12	0.24	0.20	0.13	0.08	4.9	–	–
			–			$\Sigma = 0.41$			
DBP-M5	>45	>12	0.23	0.23	0.13	0.07	4.1	776	170
			–			$\Sigma = 0.43$			

$\Sigma$  means summation of weight loss (wt%) of the propellant containing stabilizer in between 24 and 72 h.

C1 = N,N'-diethyl-N,N'-diphenyl urea, M1 = malonanilide, M2 = N,N-diethylmalonanilide, M3 = o-dinitromalonanilide, M4 = m-dinitromalonanilide, M5 = p-dinitromalonanilide.

and M5, the deflagration temperatures are 172, 172 and 170 °C, respectively. The Calorific value of DBP samples containing C1, M2, M3 and M5 stabilizers are 776, 762, 784 and 776 cal/g, respectively. The above results lead to the conclusion that the new stabilizers (M1–M5) have stabilizing effects which are comparable to C1. M2 and M3 have higher stability effects; as indicated by 3.7 and 2.8 ml of 0.05 M NaOH equivalents to the liberated nitrogen oxide gases, in comparison with 4.0 ml of the same alkali solution was required in case of C1. The M5 has nearly the same stabilizing effect like the classical stabilizer C1. Finally the M1 and M4 have little bit lower stabilizing effect as indicated by 4.3 and 4.9 ml of 0.05 M NaOH equivalent to the liberated nitrogen oxide gases in comparison with the classical stabilizer C1.

### 3.2. The Molecular orbital calculations

In order to understand the application of malonanilide and its derivatives as stabilizers for DBPs, their stabilizing effect will be correlated with many physico-chemical properties, e.g. geometrical parameters such as, electron density,  $\pi$ -bond order on different bonds, ionization potential, electron affinity, dipole moment and molecular orbital energy.

In this part, molecular orbital calculations were performed on newly prepared stabilizers such as M1–M5 and C1 as classical stabilizer. The first step is to determine the most stable form or forms of each compound using AM1 Hamiltonian. The most stable form has the minimum level of energy in the ground state.

#### 3.2.1. Ground state geometrical parameters

The MO calculations were performed on all of the studied compounds and the results e.g. of C1 and of M1 are presented in Fig. 2 that displays the optimized structures and the numbering system used for such calculations. The results obtained show that these compounds are non-planar as a result of the  $sp^3$  hybridization of the central carbon atom, while each group of CONHPh lies in one plane, which is confirmed by the values of  $\pi$ -bond order (Table 3). Table 3 shows the geometrical parameters calculated such as bond angles and bond lengths. The values of the bond angles and bond lengths are those of pure single bonds C1–C2, C2–N4, or pure double bond C=O. These data indicate the lack of conjugation extending over the whole molecule. Replacing the hydrogen atom at (NH) moiety by an ethyl group M2 does not cause appreciable changes in the values of the bond lengths,  $\pm 0.02$  Å, while the change in the bond angles is  $\pm 5^\circ$ . The steric effect of the two ethyl groups is avoided

by rotation of N–Ph group out of the plane ( $\sim 25^\circ$ ) with respect to that in case of the parent M1. The conjugation that exists at the moiety of CONHPh in case of malonanilide disappears in its ethyl derivative.

The nitro group is introduced into the phenyl ring of malonanilide to increase its activity as a stabilizer. The geometrical parameters of the most stable conformer of M3–M5 are given in Table 3. Comparison between their geometries with that of M1 showed that the nitro group has no appreciable effect on the geometry of the parent. The bond lengths and bond angles of all compounds are nearly of the same magnitude. This is attributed to the absence of the complete conjugation throughout the molecules. An important result obtained in case of M3 is the intermolecular H-bonding between H of the NH and O of NO<sub>2</sub> groups (O...H  $\sim 2.0$  Å) causing more stability of the molecule comparing to the other two isomers. Another difference is the value of angle of rotation of the two CONHPh groups with respect to each other, which is greater by about  $10^\circ$ . This difference avoids the steric hindrance between the two NO<sub>2</sub> groups.

#### 3.2.2. Ionization potential (IP) and electron affinity (EA)

The IP is the negative value of the energy level of the highest occupied, or highest partially occupied molecular orbital, in accordance with Koopmans' theorem [36]. The energy of HOMO ( $E_{\text{HOMO}}$ ) for C1 (classical stabilizer) and malonanilide compounds (M1–M5) used as stabilizers for DBPs is listed in Table 4. The magnitude of  $E_{\text{HOMO}}$  of these compounds follows the order, M2 > M1 > C1 > M3 > M4 > M5. Consequently the trend of IP required to remove the HOMO electron forming a positive ion is M2 < M1 < C1 < M3 < M4 < M5. The high value of  $E_{\text{HOMO}}$  in the case of M1 indicates its high ability for donating electrons to other substrates and it has the lowest stability effect among the studied compounds. The lower value of M5 isomer indicates that it has the lowest ability for donating electrons to other substrates. Consequently it has the highest stability effect. On the other hand, the LUMO energy,  $E_{\text{LUMO}}$ , which corresponds to the electron affinity of a compound (EA), takes the following order among these stabilizers: M5 < M4 < M3 < M1 < M2 < C1. This indicates that M5 isomer has the lowest affinity for electrons and the classical stabilizer C1 is the highest acceptor for electrons.

The energy gap ( $\Delta E$ ) is inversely proportional to the reactivity of the molecules and is usually given by Eq. (1):

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (1)$$

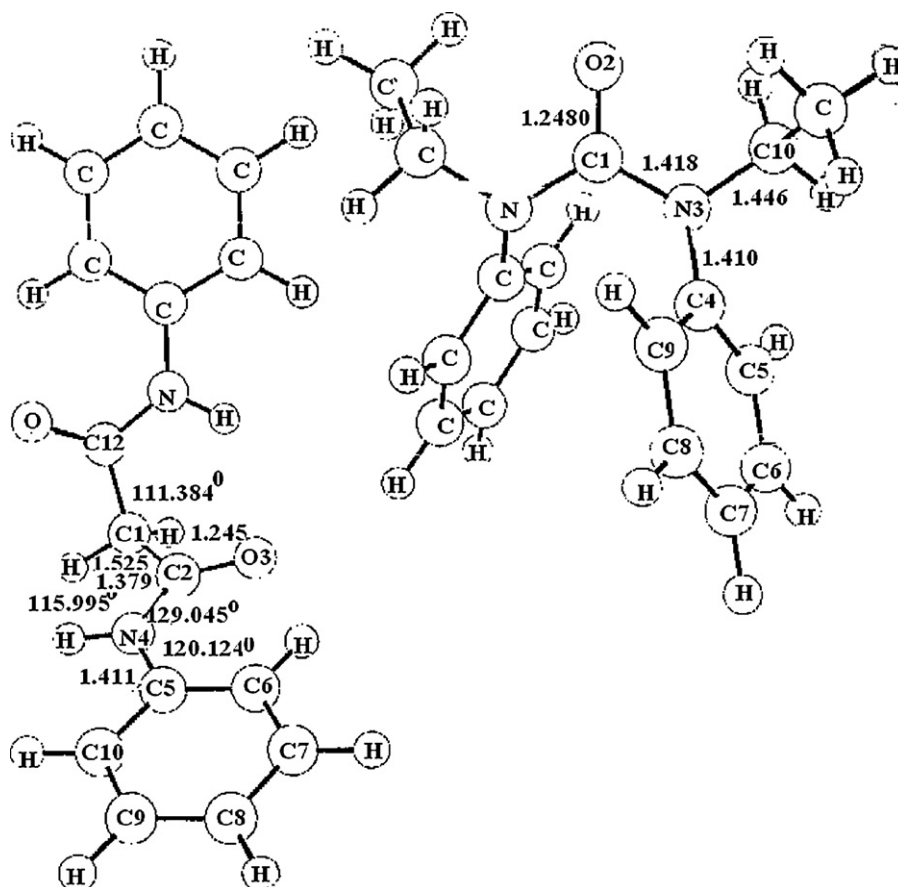


Fig. 2. Geometric representation and numbering order for the studied compounds: (a) malonanilide (M1) (b) N,N'-diethyl-N,N'-diphenyl urea (C1).

Table 3

Geometrical parameters (bond lengths (Å), and bond angles (°)) of malonanilides stabilizers.

Selected geometrical parameters	M1	M2	M3	M4	M5	C1
Bond length (Å)						
C1–C2	1.525	1.527	1.524	1.524	1.527	
C2–O3	1.245	1.245	1.243	1.243	1.243	
C2–N4	1.379	1.398	1.388	1.382	1.384	
N4–C5	1.411	1.427	1.403	1.408	1.405	
N4–C11		1.452				
Bond angles (°)						
C2C1C11	111.384	112.273	110.756	110.8	111.1	
C1–C2N4	115.995	119.615	115.846	115.9	116.0	
C2N4C5	129.045	123.758	127.919	128.9	128.9	
N4C5C6	120.142	120.198	120.381	120.1	120.1	
Net charge						
N4	–0.316	–0.274	–0.319	–0.314	–0.312	N3 –0.263
C6	–0.159	–0.161	–0.176	–0.107	–0.173	C5 –0.140
C8	–0.156	–0.156	–0.166	–0.092	–0.156	C7 0.138
C10	0.093	0.085	–0.011	0.159	0.058	C9 0.088
Total bond order						
	C2–O31.753	C2–O31.770	C2–O31.763	C2–O31.763	C2–O31.765	C1–O2 1.757
	C1–C20.909	C1–C20.991	C1–C20.916	C1–C20.916	C1–C20.916	C1–N3 0.998
	C2–N41.109	C2–N41.050	C2–N41.065	C2–N41.079	C2–N41.074	C4–N3 0.984
	C5–N41.001	C5–N40.981	C5–N41.041	C5–N41.007	C5–N41.021	C10–N30.916

C1 = N,N'-diethyl-N,N'-diphenyl urea, M1 = malonanilide, M2 = N,N-diethylmalonanilide, M3 = o-dinitromalonanilide, M4 = m-dinitromalonanilide, and M5 = p-dinitromalonanilide.

The obtained values, graphically represented by Fig. 3, show that the  $\Delta E$  values of the stabilizers take the order  $M3 < M4 < M5 < M1 < M2 < C1$ . Consequently, the expected trend of reactivity of such stabilizers will be the reverse of  $\Delta E$  i.e. **M3** will be the most reactive one.

### 3.2.3. The charge density, dipole moment and bond order calculations

The charge distribution (Table 3) on a stabilizer might be reasonably taken as an indication for locating the position of interaction between the stabilizer and propellants. It shows the charge distri-

**Table 4**  
Calculated values for  $E_{\text{HOMO}}$  (eV),  $E_{\text{LUMO}}$  (eV), energy gap  $\Delta E$  (eV), activation energy of decomposition  $E_a$  (kJ mol<sup>-1</sup>) and dipole moment ( $D$ ) for studied stabilizers.

DBPs-stabilizer mixture	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E$	Dipole moment	ml NO <sub>x</sub> gases	Weight loss (wt%)	$E_a$ (kJ mol <sup>-1</sup> ) of decomposition
DBP-C1	-9.00	0.314	9.317	2.30	4.0	80.8	93.11
DBP-M1	-8.87	-0.001	8.869	1.80	4.3	72.5	70.72
DBP-M2	-8.72	0.163	8.888	2.28	3.7	65.0	109.6
DBP-M3	-9.59	-1.267	8.327	1.46	2.8	45.9	143.43
DBP-M4	-9.67	-1.320	8.352	5.07	4.9	85.0	80.64
DBP-M5	-9.90	-1.395	8.508	7.30	4.1	48.3	139.31

\*  $E_a$  values are coming from TGA-DSC at non-isothermal conditions and calculations by Ozawa method [36].

**Table 5**  
Decomposition temperatures of DBPs samples containing different stabilizers from TGA and DTG.

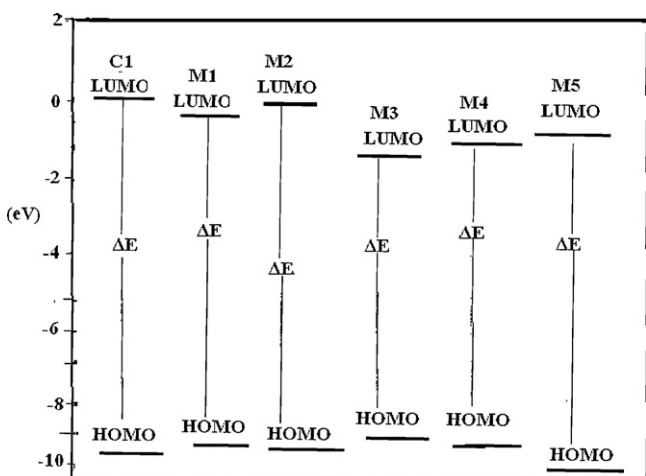
Stabilizers	Temperatures of starting decomposition (°C)	DTG peak temperatures (°C)	Rate of maximum weight loss (mg min <sup>-1</sup> )	Time difference between starting decomposition and DTG peak temperatures, °C (min)
C1	153.3	203.4	0.29	8.48
M1	153.3	201.6	0.39	8.21
M2	153.0	205.0	0.36	10.00
M3	151.5	223.0	0.53	14.70
M4	155.8	210.0	0.39	13.10
M5	156.0	221.0	0.49	11.00

C1 = N,N-diethyldiphenylurea, M1 = malonanilide, M2 = N,N-diethylmalonanilide, M3 = o-dinitromalonanilide, M4 = m-dinitromalonanilide, and M5 = p-dinitromalonanilide.

bution of M2 and M3. Generally, the highly charged atoms are O, N, C1 of the molecules and C (CON)<sub>2</sub> group. The substituents N-ethyl or NO<sub>2</sub> decrease only the charge on N or C atoms to which they are directly attached.

The dipole moment values are calculated for different compounds (Table 4) from which it indicates, that p-dinitro isomer (M5) has the largest value (7.298 Debye) implying a high extent of charge separation. The reverse is found in case of o-dinitro isomer (M3) which has the lowest value of dipole moment (1.458 Debye).

The value of bond order of any bond is a measure of its strength. This value depends on the position of the bond in a moiety of the molecule. The calculated total bond orders and the corresponding  $\pi$ -components are given, for C1 and M1–M5 (Table 3). The values obtained are relatively low indicating low  $\pi$ -characters of most bonds. The bond order value corresponding to C1–C2 bond is larger for the N-alkylated compounds C1 and M2 when compared with the other stabilizers. The  $\pi$ -bond order values of C2–N4 and N4–C5 bonds depend on the type of substituent and its position. The  $\pi$ -bond order values in case of C1 as a classical stabilizer are low compared with the values of new stabilizers.



**Fig. 3.** Schematic diagram for  $\Delta E$  gap for different stabilizers: C1 = N,N'-diethyl-N,N'-diphenyl urea, M1 = malonanilide, M2 = N,N-diethylmalonanilide, M3 = o-dinitromalonanilide, M4 = m-dinitromalonanilide, M5 = p-dinitromalonanilide.

**Table 6**  
DSC results of DBP samples containing different stabilizers in comparison with TG losses within the decomposition temperature range ( $T_f$ – $T_i$ ).

Stabilizers	$T_i$ (°C)	$T_m$ (°C)	$T_f$ (°C)	% weight loss
C1	162.0	189.1	210.7	80.8
M1	159.0	186.8	213.2	72.5
M2	160.2	191.7	210.9	65
M3	151.1	189.8	209.3	45.9
M4	156.5	188.2	227.3	85
M5	155.6	190.4	210.7	48.3

$T_i$  = temperature of starting decomposition,  $T_m$  = peak temperature and  $T_f$  = temperature of ending decomposition.

### 3.3. Correlation between quantum chemical calculations and practically measured thermal stability of stabilizers and DBPs containing stabilizers

The ability of malonanilides to act as stabilizers may be attributed to their physico-chemical properties. It is apparent that such quantities like charge density on the various atoms, the bond order, the dipole moment, the ionization potential, the electron affinity and energy gap ( $\Delta E$ ) play an important role in such behavior. The calculated quantum chemical values (Table 4) for these stabilizers were used to correlate and interpret the experimentally measured thermal stability of the studied stabilizers and the DBP samples containing these stabilizers. Therefore, this correlation is subdivided into two parts.

#### 3.3.1. Thermal stability of stabilizers and its correlation with ground state parameters

As previously mentioned the experimentally measured thermal stability factors by different tests for various stabilizers refer to the decrease of their thermal stability in the order: M5 < M3 < M4 < M2 < M1 < C1. To explain this thermal behavior, quantitatively in a more efficient way, thermo-gravimetric data, TG weight losses wt% (Tables 5 and 6) and DSC data (Table 7), the quantum mechanical calculated values; ionization potential ( $E_{\text{HOMO}}$ ), the electron affinity ( $E_{\text{LUMO}}$ ), energy gap ( $\Delta E$ ), the  $\pi$ -bond order, and charge densities are correlated with the different experimental stabilizing parameters e.g. the volume of NO<sub>x</sub> weight loss percent and Ozawa activation energy of decomposition,  $E_a$  (kJ mol<sup>-1</sup>) [35].

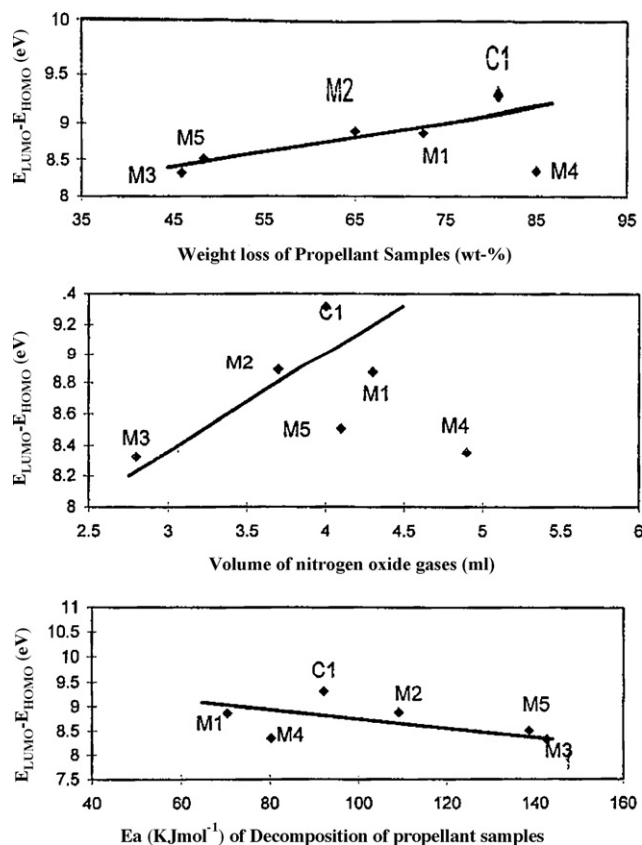


Fig. 4. Relation between the HOMO–LUMO energy gap and the stabilizing effect of different stabilizers (C1, M1–M5).

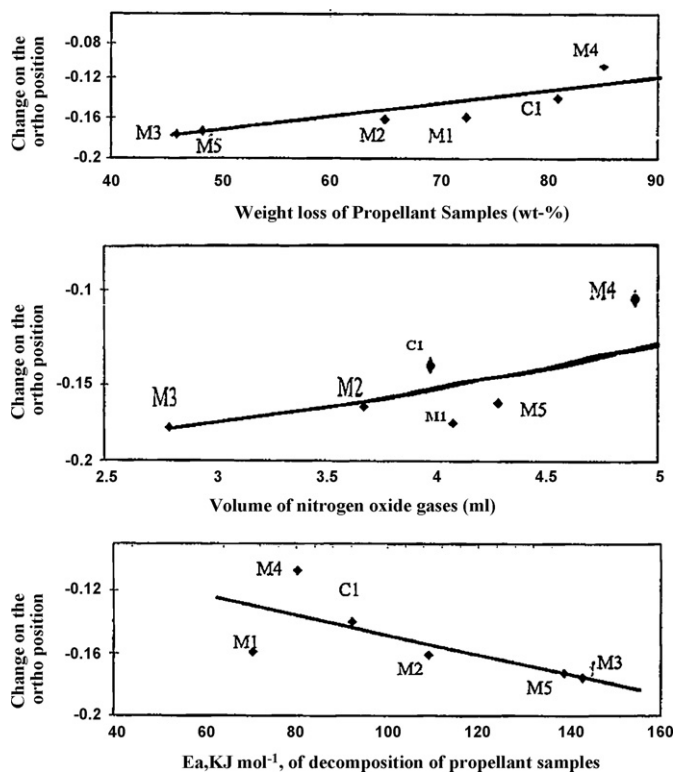


Fig. 5. Relation between the net charges on ortho positions (C6/C5) and stabilization effect of different stabilizers (C1, M1–M5).

Table 7

The kinetic parameters of the thermal decomposition of propellants samples containing different stabilizers from non-isothermal TGA.

Added stabilizer	Activation energy ( $KJ mol^{-1}$ )	Frequency factor ( $min^{-1}$ )	Order
C1	93.11	$1.03 \times 10^{10}$	0.8
M1	70.72	$5.64 \times 10^6$	0.6
M2	109.6	$1.96 \times 10^{11}$	0.7
M3	143.43	$1.48 \times 10^{15}$	1.5
M4	80.64	$5.83 \times 10^7$	0.0
M5	139.31	$2.26 \times 10^{14}$	1.2

The results are shown in Figs. 4–7, from which it is noticed that,

- The value of bond order of any bond is a measure of its strength.  $\pi$ -bond order values of different bonds are low; indicating low  $\pi$ -character of most bonds, leading to a certain bond weakening.
- The lowest  $\pi$ -bond order values are those of the classical stabilizer C1 bonds, explaining the weakening of its bonds comparable to the new ones. Therefore, its lower thermal stability can be expected.
- Amongst the new stabilizers, the weakest bond is the C1–C2 bond which has the lowest  $\pi$ -bond order. Therefore, a certain reactivity of this bond can be expected.
- M2 has the lowest  $\pi$ -bond order values between the new stabilizers (0.225, 0.098), while the introduction of nitro groups can lead, however, to an enhanced reactivity at certain positions and therefore to reduced compatibility.

### 3.3.2. Thermal stability of DBPs containing stabilizers and its correlation with calculated parameters

The correlation between the ( $E_{HOMO}$ ), ( $E_{LUMO}$ ), energy gap ( $\Delta E$ ), and charge densities of the stabilizers and volume (ml) of  $NO_x$ ,

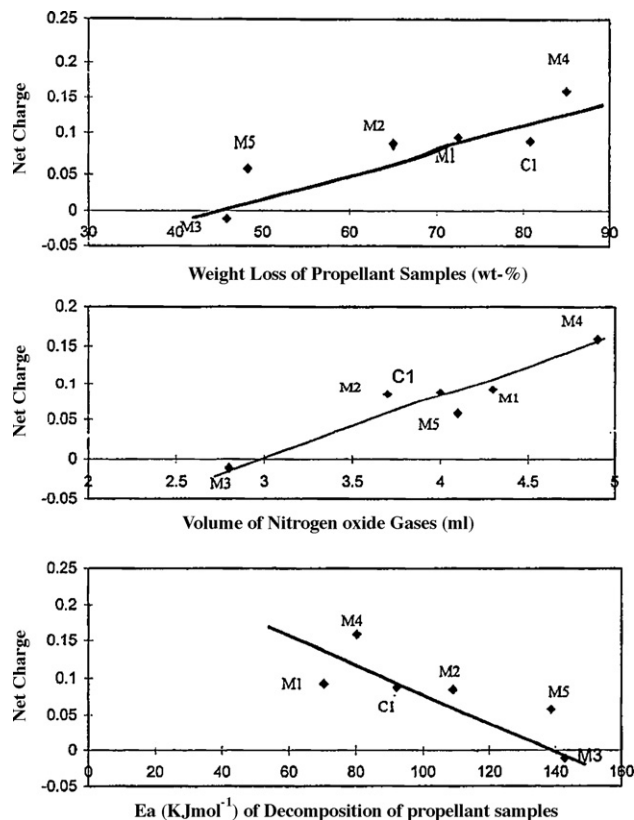


Fig. 6. Relation between the net charges on ortho positions (C10/C9) and stabilization effect of different stabilizers (C1, M1–M5).

non-isothermal TG weight loss (wt%) and activation energies  $E_a$  ( $\text{kJ mol}^{-1}$ ) [36] calculated according to Ozawa method, of decomposition of propellant samples containing different stabilizers describe the stabilization effects of the studied stabilizers. These data are given in Table 4. The stabilization effect decreases with the increase of  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  i.e. with the decrease of the ionization potential (IP) and consequently the direction of easy ionization of molecules. The correlation between the  $E_{\text{HOMO}}$  and  $E_a$  of decomposition is better than the random relation with the volume of  $\text{NO}_x$  gases evolved.

The correlation between the energy gap  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$  and the stability effect of studied stabilizers can be expressed as an activation energy,  $E_a$  ( $\text{kJ mol}^{-1}$ ) [35], of decomposition of propellant samples. Their weight loss % and the volume of  $\text{NO}_x$  gases are shown in Table 4. It is known that  $\Delta E$  is inversely proportional to the reactivity of the molecule [36]. These data show that as  $\Delta E$  decreases, the activation energy of the propellant sample increases; while the volume of nitrogen oxide gases liberated decreases and the weight loss of the propellant samples decreases i.e. stability effect increases. **M3** which has the lowest  $\Delta E$  value has a high reactivity against  $\text{NO}^+$  ions liberated and accordingly it has the high ability to stabilize DBPs.

The correlation between the net charge on o- or p-position or the concentrated charge on the benzene ring with stabilization effect is represented by data in Table 3 and by Figs. 5 and 6. Different mechanisms were suggested to explain the role of different stabilizers in stabilizing the propellants [37–40]. It was assumed that the first step is the reaction of  $\text{NO}^+$  produced from nitrocellulose decomposition with the nitrogen atom of the stabilizer to form N-nitroso derivative as given by Eqs. (2–4):



where  $\text{y} = \text{NO}_3^-$  and  $\text{NH}$  = the stabilizer moiety.

The second step is the rearrangement of the formed N-nitroso to C6–NO or C6–NO<sub>2</sub> of the benzene ring [41–44]. Therefore the charge on N-atoms and the factors increasing its value have an important role in fixation of nitrogen oxides on the stabilizer.

Figs. 5 and 6 represent the charge distribution e.g. of **C1** and **M1**. The high negative charges are concentrated on the oxygen atom of the CO group and on the nitrogen connected to the ring (center of attack). The magnitude of charge density on nitrogen atom is found to be high in case of **M3**, while it is of low density in case of **C1** as a classical stabilizer. Consequently, the first step in the suggested mechanism will be fast in case of new stabilizers more than the classical one and **M3** will be the fastest one. The order of negative charge density on the nitrogen atoms for such compounds follows the sequence; **M3** > **M1** > **M4** > **M5** > **M2** > **C1**.

The charge on the o- and p-position as the active sites depends on the presence of the substituent and its position. The negative charge decreases in the following order, **M3** > **M5** > **M2** > **M1** > **C1** > **M4**; for C6/C5 which is the trend of their stabilization effect (Figs. 5 and 6).

The same correlation is obtained but with the net charge on C10/C9 of the benzene ring of the stabilizers. Again **M3** shows the highest value of negative charge (–0.011) while **M4** shows the highest positive value of the charge (0.159). The correlation between the net charge on the benzene rings and parameters measured for the stabilization effect is shown in Table 4; a good correlation is obtained. Comparison of the results obtained show that the high electron charge on N atom of the stabilizers and on its benzene ring is the most important factor, but it is not the only factor governing the stabilization effect of the stabilizers.

## 4. Conclusion

The use of thermal stability tests (qualitative and quantitative) for double-base propellants containing both classical (**C1**) and newly prepared stabilizers (**M1–M5**) can distinguish between their stabilization effects. But it is appropriate to use theoretical MO calculation parameters to confirm such differentiations. This combination gives a complete assessment of the more efficient stabilizers and the main reasons for their stabilization effect on the studied DBPs. The combination of experimental thermal degradation and theoretical MO-calculations usually gives more expressive conclusions [45,46] than just the use of practical techniques.

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