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Synthesis, Structure and Translations of 2-(2-Substitutedphenyl) Hydrazone) 5,5-Dimethylcyclohexane-1,3-Dione

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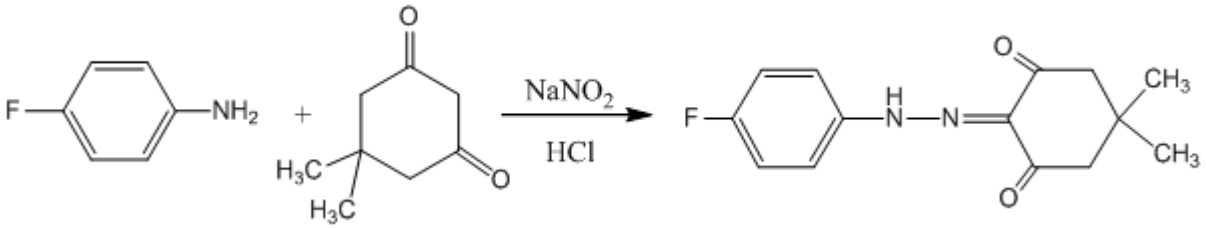
The diazotization reaction of different aromatic amines with 5,5-dimethylcyclohexane-1,3-dione were investigated, sythesized compounds were reacted with ethylenediamine and structures were confirmed with the method of X-Ray.

Keywords: *β- diketones, hydrazones, keto hydrazone form, X-Ray.*

Different β-diketones and their complexes are widely used as biologically active compounds [1-2]. It is also known that, substitutedreagents and laser chelates ofthese compounds [3], chemical and photochemical catalyst [4] of the biologically active derivatives are usedto treat inflammatory diseases [5]. We have been investigated diazotization of different aromatic amine by using benzoicacetophenone [6], in this research 5,5-dimethylticyclohexane-1,3-dione has been taken as an object and the synthesis of 2- (2- (4-fluorophenyl) hydrazone)-di-methyltricyclohexane1,3-dion(I) was shown following scheme.



(I)

The reaction was monitored by thin layer chromatography method. (Sorbfil). The structure of the compound was approvedbyRSA, and it was determined that, the crystal form ofthis compound doesexist as keto hydrazon form.

The triclinic structure of 2- (2- (4-fluorophenyl) hydrazone) -5,5-dimet-hylcyclohexane-1,3-dione (I) was deposited at theThe Cambridge Crystallographic Data Centre (CCDC 1475293).The cage angels of combination a=5.993(2)Å b=10.446(4)Å, c=10.731(4)Å, $\alpha=97.765(8)^0$, $\beta=102.860(8)^0$, $\gamma=98.925(8)^0$, space group P-1,Z=2; V=637.0(4) $Å^3$, $D_x=1.368$ Mg/m^3, $\mu= 0.102$ mm^{-1}. Crystal sizes 0.330 x 0.260 x 0.220 mm^3.

The molecular structure of compound (I)is shown below.

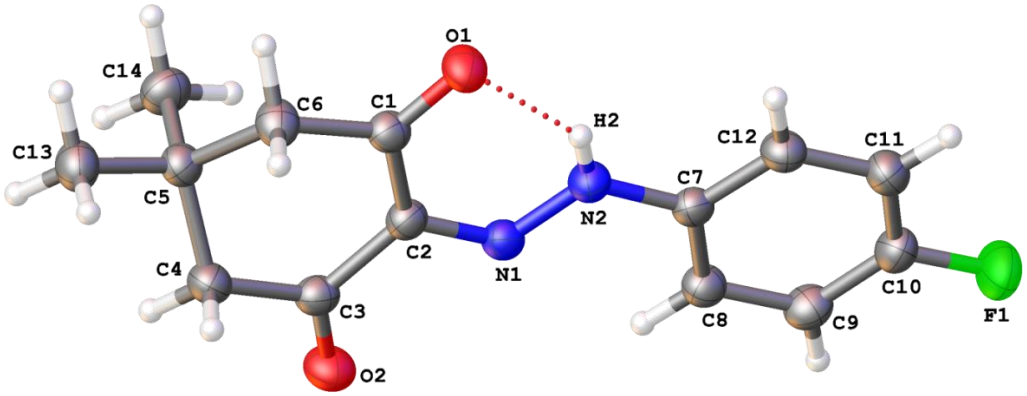
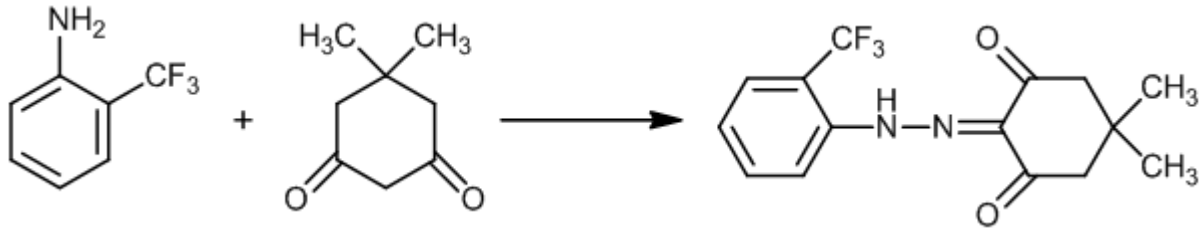


Figure1. *Molecule structure of 2-(2-(4-fluorphenyl) hydrazone)-5,5-dimethilcyclohexane-1,3-dione (I).*

To continue the researchs, we were synthesized 2- (2- (2-trifluoromethylphenyl) hydrazone)-5,5-dimethylcyclohexane 1,3-dione (II). Scheme is shown below:



(II)

The reaction was monitored by thin layer chromatography method (Sorbfil).The monoclinic structure of 2- (2- (4-fluorophenyl) hydrazone) -5,5-dimethylcyclohexane-1,3-dione (II) was deposited at the The Cambridge Crystallographic Data Centre(CCDC 1484656).The cage angels of combination a=15.5610(12)Å, b=6.1069(5)Å, c=15.6267(12)Å, β=97.3588(13)^0, V=1472.8(2) Å^3, Z=4, space group P2$_1$/n, D$_x$=1,315mq/sm^3, μ= 0.120 mm^{-1} , Crystal sizes0.630 x 0.220 x 0.150 mm^3.

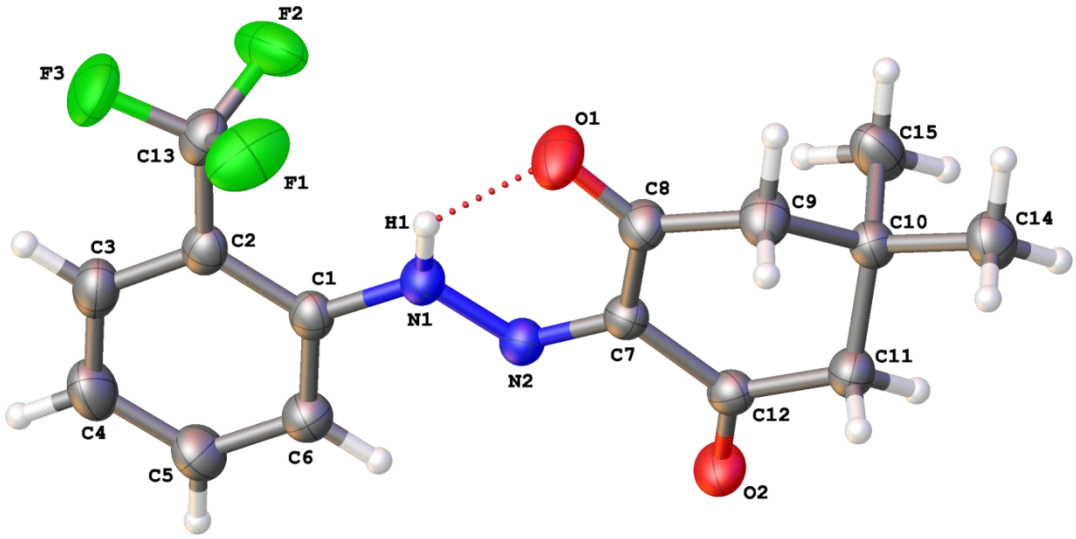
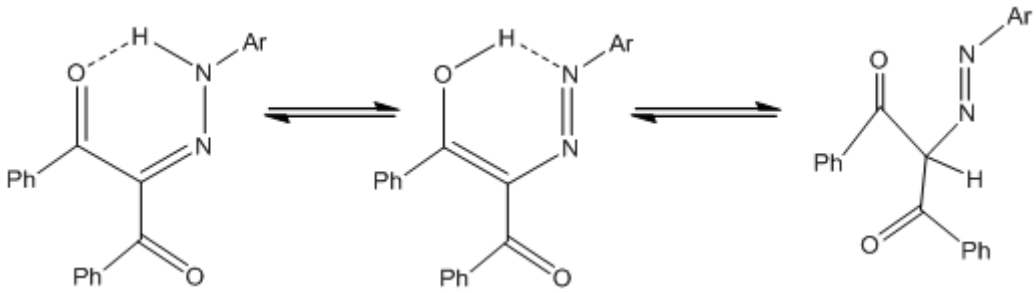


Figure2. *Molecule structure of 2- (2- (2-trifluoromethylphenyl) hydrazone) -5,5-dimethylcyclohexane 1,3-dione (II).*

It is known that,ketohydrazone (KH), azo ketone (AK) and azo enol (AE) tautomeric forms are characterized for hydrazones.

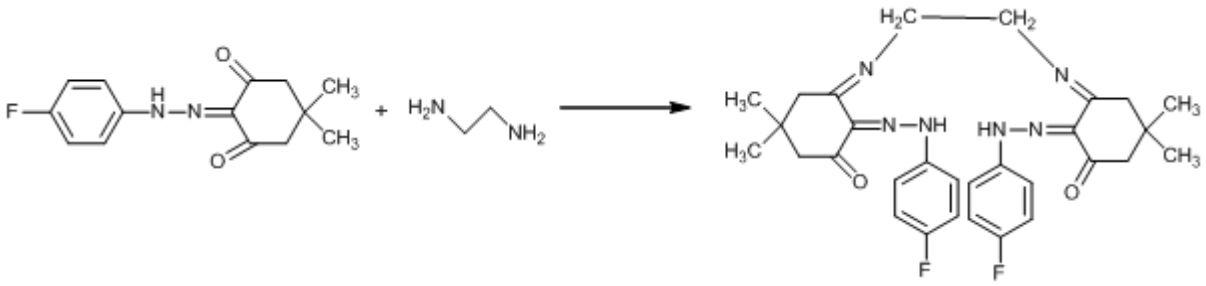


KH **AE** **AK**

We were intestigated structureof these compounds in "Bruker APEX II CCD"diffractometeron the other hand it sholud be pointed out that,crystallineformof synthesized compounds exit as keto hydrazone form (KH).

In our previous researches, we weresynthesized6- (2- (4-substitutedhalogenphenyl) hydrazone)-5,7-diphenyl-3,6-dihydro-2H-1,4-diazepine from 6- (2- (4-substitutedhalogenylphenyl) hydrazone)-1,3-diphenylpropane-1,3-dionesreaction with ethylenediamine(2:1)and the structure are confirmed with the method of RSA [7].

The reaction between ethilendiamineand 2- (2- (4-fluorfenil) hydrazone) -5,5-dimethylcyclohexsane 1,3- dion (I) 2: 1were investigated, on the second hand it was determined that, (3Z, 3′Z)-3,3′- (ethane-1,2-dibis (azanililden))bis(2- (2-4-fluorphenyl) hydrazone)-5,5-dimethylcyclohexsanon (III) was obtainedpresence of an acid the scheme of this reaction can be represented below by the following scheme.



(III)

The monoclinic structureof (3Z, 3′Z)-3,3′- (ethane-1,2-dibis(azanililden))bis(2-(2-4-fluorphenyl) hydrazone)-5,5-dimethylcyclohexsanon (III)was deposited at the The Cambridge Crystallographic Data Centre(CCDC 1510185). The cage angels of combination C2/c a=22.7715(19)Å, b=17.2794(15)Å, c=25.639(3)Å, β=112.2966(12)^0; Z=2; V=9334.3(16) Å^3; D_x=1.217 Mg/m^3 , μ= 0.089 mm^{-1}, Crystal sizes0.360 x 0.160 x 0.110 mm^3.

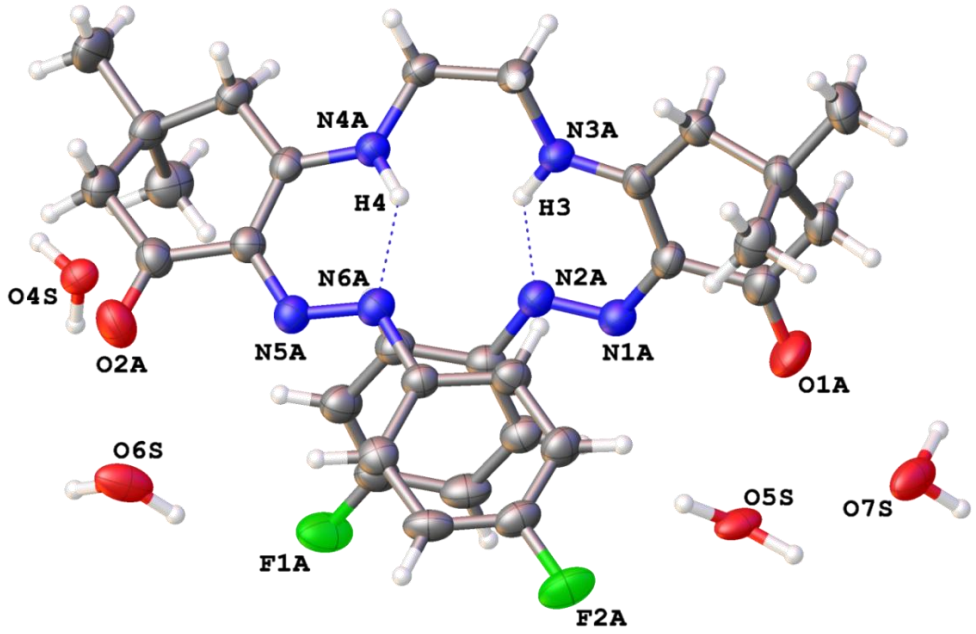


Figure3. *Molecule structure of(3Z, 3′Z)-3,3′- (ethane-1,2-dibis(azanililden))bis(2-(2-4-fluorphenyl) hydrazone)-5,5-dimethylcyclohexsanon (III)*

Experimental part

The reaction and the purity of the substanceswas monitored by TLC(*Sorbil*). The structure of substances are studied with "Bruker APEX II CCD"difractometer (T = 100 K, λMoK$_\alpha$-radiation, graphit monochramator, φ- və ω-scannered, $2\theta_{max} = 56^0$).

The general method of synthesis 2-(2-(substitutedphenyl) hydrazone)-5,5-dimethylcyclohexane-1,3-diones(I-II)

0,0625 mol aromatic amine and0,35 gr KOH are dissolved in distilled water in the threenecked flask. 0.0225 mol $NaNO_2$ was dissolved in 2 ml distilled water and was added to the mixture then left it to stir under magnetic stirrer bar . 2ml HCl was added drop by drop to the mixture and left to stir 30min under 0^0Ctemperature .Later, 0.0625 mol 5.5-dimethylcyclohexane-1,3-dione and 0.5125 gr CH_3COONa were dissolved in 10 mlC_2H_5OH and the temperature of the mixture was decreased 0^0C temperature then added drop by drop to the previous mixtureand left it to stir 1 h under 0^0C.The product is filtered and again recrystallized in ethanol.

2- (2- (4-fluorophenyl) hydrazono) -5,5-dimethylcyclohexane 1,3-dione (I)**(**Yield74%), $T_{m.p}$= 198-200^{0}C.$C_{14}H_{15}N_2O_2F$; Calculated for(%): C 64,12; H 5,72; N 10,68; F 7,25. Found (%): C 64,21; H 5,59; N 10,71, F 7,15.^{1}H-NMR (DMSO-d_6) δ,m.h.; 0.97-1.09 (6H, $2CH_3$), 2.64-2.71 (4H, $2CH_2$), 6.61-6.99 (4H, CH-Ph), 8.21 (1H, NH).^{13}C-NMR (DMSO-d_6) δ,m.h.;26.92 ($2CH_3$), 30.61 (C)50.51-51.12 ($2CH_2$), 11.99-116.58 (4CH, Ph), 137.91 (C=N), 137.9 (C-NH), 156.92 (C-NH), 156.92 (C-F), 187.23 (2CO).

2- (2- (2-trifluoromethylphenyl) hydrazono)-5,5-dimethylcyclohexane 1,3-dione (II).**(**Yield 73%), $T_{m.p.}$= 100-102^{0}C. $C_{15}H_{15}N_2O_2F_3$;Calculated for (%): C 57,69; H 4,80; N 8,97; F 18,26 Found (%): C 57,79; H 4,65; N 8,73; F 18,42.^{1}H-NMR (DMSO-d_6) δ,m.h.; 0.97-1.06 (6H, $2CH_3$), 2.64-2.69 (4H, $2CH_2$), 6.55-7.49 (4H, CH-Ph), 8.16 (1H, NH).^{13}C-NMR (DMSO-d_6) δ, m.h.;26.71-27.12 ($2CH_3$), 29.94 (2C),50.2-51.6 ($2CH_2$), 119.1-133.2 (4CH-Ph), 135.49 (C-CF_3), 137.34 (C-NH), 137.72 (C=N), 125.4 (CF_3), 187.01 (2CO).

Synthesis of (3Z, 3′Z)-3,3′- (ethane-1,2-dibis(azanililden))bis(2-(2-4-fluorphenyl) hydrazone)-5,5-dimethylcyclohexsanon (III). 2 mmol 2- (2- (4-fluorophenyl) hydrazono) -5,5-dimethylcyclohexane 1,3-dione are dissolved 15-20 ml of ethanol in the threenecked flask. 1 drop HCl was added and the mixture was heated till 50^{0}C.Then 1 mmol ethilendiamine was addded and left it to stir 1h under magnetic stirrer bar. Obtained (3Z, 3′Z)-3,3′- (ethane-1,2-dibis(azanililden))bis(2-(2-4-fluorphenyl) hydrazone)-5,5-dimethylcyclohexsanonis filtered and purified by the method of re-crystallization. **(**Yield 59%) $C_{30}H_{34}N_6O_2F_2$;Calculated for (%): C 65,93; H 6,22; N 15,38; F 6,59 Found (%): C 65,77; H 6,41; N 15,52; F 6,50.СЯМР ^{1}H-NMR (DMSO-d_6) δ,m.h.;0.99-1.08 (12H, $4CH_3$), 1.43-1.49 (4H ,$2CH_2$), 2.61-2.69 (4H, $2CH_2$), 2.69 (4H, 2CH-N), 6.63 (4H, CH-Ph), 6.94 (4H, CH-Ph), 8.47 (2H, NH). ^{13}C-NMR (DMSO-d_6) δ,m.h.; 26.51-27.12 ($4CH_3$), 30.41 (2C)41.93-50.21 ($4CH_2$), 62.91-62.71 ($2CH_2$–N), 115.31-116.52 (8CH-Ph), 137.71 (2C=N-NH), 138.61 (2C-NH), 155.23 (2C=N-CH_2), 157.14 (2C-F), 186.45 (CO).

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