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Aromatic Aldehyde Methylhydrazones and Nitrile Oxide. Crystal Structure of 3,6-Diphenyl-4-methyl-6H-1,2,4,5-oxatriazine.

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Abstract: *The reaction of methylhydrazones 1 with nitrile oxide has been examined. The initial product is the Z-adduct 2, which, depending on the reaction procedure and the substituents, can undergo either isomerization to the thermodynamically stable E-adduct 3 or tautomerization to the oxatriazine 4 or irreversible cyclization to the triazole 5. A general mechanism consistent with these results is proposed Structure 4 was confirmed by X-ray studies*

Some time ago during our studies on the reactions of nitrile oxides with nucleophilic compounds we reported[1] that methylhydrazones **1** and benzonitrile oxide (BNO) give 1H-1,2,4-triazoles **5**, either directly or after acid-catalyzed cyclization of the isolated E-hydrazoximes **3**. Subsequently, on the same reaction Hussein and co-workers reported[2] different results and disproved the 1,2,4-triazole structure assigned by us for such reaction products. According to the Baldwin rules,[3] they concluded that 1,2,4,5-oxatriazines **4**, which derived from a favored endo-6-trig process, are the exclusive cyclization products of the initial nonisolable Z-adducts. This appeared a surprising assertion, since the 1,2,4-triazole structure had been unambiguously confirmed. Thus, in order to give a full account of the observed formation of the triazole and oxatriazine systems, we decided to review the reaction between hydrazones and nitrile oxides in more detail and herein we report the results of our study.

Results and Discussion

For this investigation we used methylhydrazones **1**, which were reacted with BNO following both our procedure[1] and that of Hussein. Under our reaction conditions all attempts to prepare oxatriazines **4** were unsuccessful. In fact, the reaction of **1** with the nitrile oxide in refluxing ether followed by chromatographic separation of the products using a column of silica gel (el. chloroform) gave exclusively triazoles **5**, with the exception of **1f** which gave the corresponding E-hydrazoxime **3f**. Using Hussein's method - reaction of **1** in $CHCl_3$ at -20° with BNO generated in situ from benzohydroxamoyl chloride and triethylamine -, but separating the reaction products by chromatography as above, the same compounds **5** and **3f** were obtained. The structure of **5** was based on the analytical and spectroscopic data and confirmed by chemical evidence and by comparison with an authentic sample (Experimental).

When separation of the products was carried out by crystallization in the cases of **1a**, **1b** and **1e** the expected oxatriazines **4** were isolated, and their spectroscopic properties were identical to those described,[2] except for the ^1H NMR coupling constant $J_{C6H,NH}$ (11Hz against 5Hz). Instead, even using the same procedure as Hussein, **1c** and **1d** failed to give the corresponding oxatriazines **4**: we obtained a non-separable mixture of **2** and **3** isomers and of **2** and **4** tautomers, respectively. In case f, the E-oxime **3** was the sole product observed. The Z-form **2** is readily distinguished from the E- **3** and ring-form **4** by the position of the N-methyl protons in the ^1H NMR spectra (Table 1). In the case of c, in chloroform solution, **2** is initially present as pure Z-isomer, this however tends to slowly transform into the more thermodynamically stable[4] E-isomer **3c**, as shown by the appearance of a new signal for the N-Me in the ^1H NMR spectra. In the case of d, **2** was also observed as a single Z-isomer, but this, unlike **2c**, goes into tautomeric equilibrium with the corresponding oxatriazine **4** a few minutes after preparation of its solution in chloroform. This same phenomenon is observed when recording the ^1H NMR spectra of oxatriazines **4a**, **4b** and **4e**: these clearly show the constant presence of their open-chain precursor, that is, the Z-hydrazoxime **2a**, **2b** and **2e**. In fact, in each spectrum there is a singlet in the range δ 3.25-3.41 and another in the range δ 7.61-7.83 which originate respectively from N-Me and from azomethine proton of the open-form **2**, and again a singlet in the range δ 2.87-2.90 and two doublets centered in the range δ 4.52-4.28 and 5.39-5.25, respectively assignable to the N-Me and to the NH and C_6H of the closed-form **4**. The former doublet disappears upon addition of D_2O, while the latter collapses to a singlet. The ring-chain tautomeric ratio **2/4**, calculated from the relative intensities of the respective NMe ^1H NMR signals at room temperature, is 15/85%. In all cases, such equilibria don't vary appreciably and can be observed even after a time period of 12, 24 hours or a week after preparation of the relative solutions.

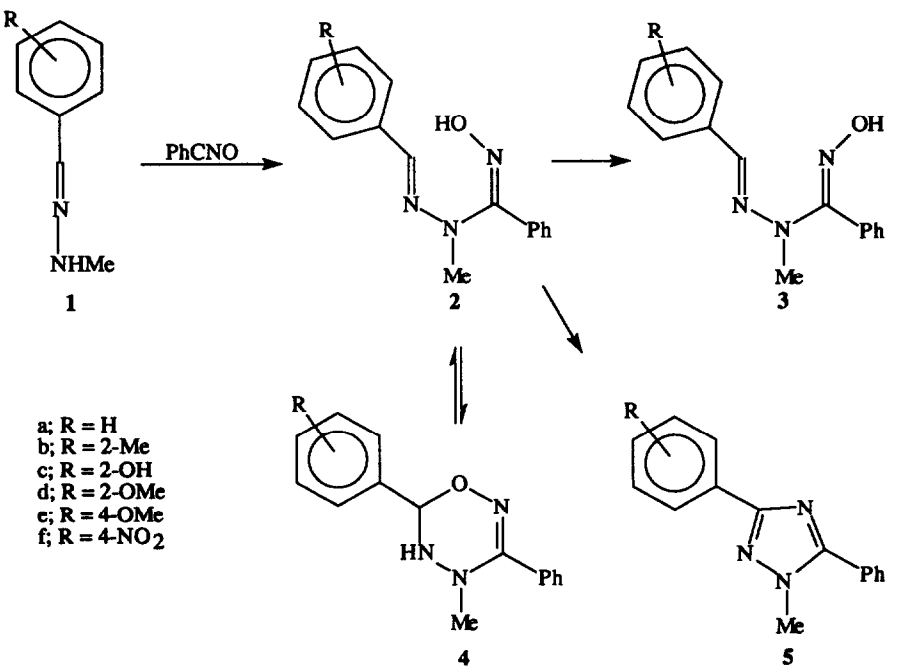
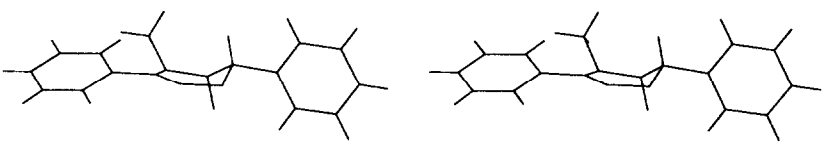


Table 1. Selected ^{1}H NMR data[A] for **2**, **3**, **4** and **5**

	Z-form **2**	ring-form **4**			E-form **3**	triazole **5**
Compd	CH_3-N	CH_3-N	C_6-H(d)[B]	N-H(d)[B]	CH_3-N	CH_3-N
a	3.35	2.87	5.35	4.28		4.00
b	3.38	2.90	5.36	4.14		4.00
c	3.41[D]				3.52[C]	3.97
d	3.31	2.87	5.39	4.52		3.95
e	3.25	2.87	5.25	4.22		4.00
f					3.55[C]	

[A]Recorded in $CDCl_3$. [B]J=11 Hz [C]Unaltered on silica gel. [D]Transformed entirely in the corresponding **5** after treatment on silica gel.

The structures of the hydrazoximes **2** and **3** were assigned on the basis of their spectroscopic data and confirmed by the cyclisation reactions. The structure of the oxatriazines **4**, based on the spectroscopic and analytical data, was confirmed by an X-ray crystallographic analysis carried out on **4a**. The figure shows the molecular conformation of **4a** with the numbering scheme for the atoms and with dotted lines showing the hydrogen bonds. Bond distances, angles and some relevant torsion angles are listed in Table 2. The asymmetric unit consists of two nearly identical stereoisomers (S) at C1 and C21. The oxatriazinic rings adopts half-envelope-type conformation as can be seen from the stereoscopic molecular frame.



The aromatic ring (C19, C14, C15, C16, C17, C18) with normal geometry 1.385 Å and 120° for the average bond length and average internal angle, is linked to sp^2 C4 (C14-C4 1.483(5)Å) and has an angle of 41.1(1)° in relation to the oxatriazinic ring. The corresponding ring (C34, C35, C36, C37, C38, C39) linked to sp^2 C24 (C34-C24 1.481(5)Å) has an angle of 39.3(1)° in relation to the central oxatriazinic ring. These dihedral angles in both the molecules indicating no π-delocalization from the phenyl rings to the oxatriazinic ring {C4-N3, 1.294(4)Å; C24-N23 1.304(5)Å}. The torsion angles for C19-C14-C4-N3 and C39-C34-C24-N23 are 43.9(5)° and 38.8(5)° respectively. The strong steric interactions between the phenyl rings and the methyl groups bonded to N5 and N25 {C7-N5 1.469(4)Å and C27-N25 1.465(4)Å} are responsible for the prevention of π-delocalization. The other phenyl rings are linked to the oxatriazinic ring through asymmetric sp^3 carbon atoms: C8-C1 1.507(5)Å C28-C21 1.506(5) Å. The torsion angles C9-C8-C1-O2, 31.2(4)°; C13-C8-C1-N6, 89.6(4)°; C29-C28-C21-O22, 37.0(3)° and C29-C28-C21-N26, 94.0(4)° are the most significant difference between the two molecules present in the asymmetric unit. Inside the oxatriazinic ring the bond distances: N3-O2 1.420(4)Å, O2-C1 1.435(2), C1-N6 1.440(5)Å, N6-N5 1.419(4)Å, N5-C4 1.380(4)Å, C4=N3 1.294(4)Å and the bond angles C1-O2-N3 113.7(3)°, O2-C1-N6 111.6(3)°, N5-C4-N3 126.7(3)° are equal within the e.s.d.s. to the corresponding values of the second molecule. The nitrogen-nitrogen bond distances N6-N5 1.419(4)Å and N26-N25 1.432(4)Å are comparable with the value of 1.411(2)Å reported for the single bond N-N in the compound 5-

(4-Methoxyphenyl)-3,4-dimethyl-6-(4-nitrophenyl)-2H-1,3,4-oxadiazin-2-one[5] where the N-C(Me) bond distance is also comparable to that found in the present compound. The most notable features are the torsion angles: H1-C1-N6-H6 178.4(4)° and H21-C21-N26-H26-175.4(4)°; which are consistent with NMR data. Bond lengths and angles for the asymmetric C1 and C21 are consistent with accepted values for sp^3 carbon atoms.The molecular packing is essentially due to van der Waals interactions. There are also several C···C, C···N, C···C, N...N and O···N inter and intramolecular contacts less than the sums of the van der Waals radii. Some of these can be properly described as hydrogen-bonds as can be seen from the figure where these bonds are represented with dotted lines.

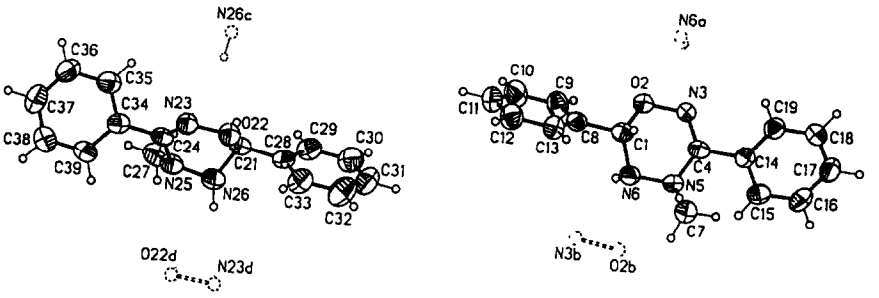


Figure. A perspective view of the molecular structure with crystallographic numbering scheme and hydrogen bonds

Table 2.

Bond lengths (Å)

C1-O2	1.435(4)	C21-O22	1.425(4)	C9-C1	1.382(6)
C1-N6	1.440(5)	C21-N26	1.450(5)	C10-C11	1.370(6)
C1-C8	1.507(5)	C21-C28	1 506(5)	C11-C12	1.372(6)
O2-N3	1.420(4)	O22-N23	1.426(4)	C12-C13	1.387(6)
N3-C4	1.294(4)	N23-C24	1.304(5)	C14-C15	1.395(6)
C4-N5	1.380(4)	C24-N25	1 372(5)	C14-C19	1.389(5)
C4-C14	1.483(5)	C24-C34	1.481(5)	C15-C16	1.377(6)
N5-N6	1.419(4)	N25-N26	1.432(4)	C16-C17	1.373(7)
N5-C7	1.469(4)	N25-C27	1.465(4)	C17-C18	1.376(6)
C8-C9	1.387(5)	C28-C29	1.379(5)	C18-C19	1.375(6)
C8-C13	1.379(5)	C28-C33	1.384(5)	C38-C39	1 371(6)
C37-C38	1 370(8)	C36-C37	1.361(7)	C35-C36	1 392(6)
C34-C39	1.394(6)	C34-C35	1.379(6)	C32-C33	1.379(6)
C31-C32	1.357(6)	C30-C31	1.371(6)	C29-C30	1.381(6)

Bond angles (°)

N6-C1-C8	112.3(3)	N26-C21-C28	111.7(3)	C11-C12-C13	121.1(4)
O2-C1-C8	107.1(3)	O22-C21-C28	107.7(3)	C8-C13-C12	119.7(3)

O2-C1-N6	111 6(3)	O22-C21-N26	111 7(3)	C4-C14-C19	120.6(3)
C1-O2-N3	113.7(2)	C21-O22-N23	113 2(2)	C4-C14-C15	120 3(3)
O2-N3-C4	116 4(3)	O22-N23-C24	116 1(3)	C15-C14-C19	119 0(3)
N3-C4-C14	114 8(3)	N23-C24-C34	114 2(3)	C14-C15-C16	119 7(4)
N3-C4-N5	126 7(3)	N23-C24-N25	127.1(3)	C15-C16-C17	121.1(4)
N5-C4-C14	118.1(3)	N25-C24-C34	118.4(3)	C16-C17-C18	119.2(4)
C4-N5-C7	119 3(3)	C24-N25-C27	118 8(3)	C17-C18-C19	120 9(4)
C4-N5-N6	115.9(3)	C24-N25-N26	115 6(3)	C14-C19-C18	120 1(4)
N6-N5-C7	111 0(3)	N26-N25-C27	111.3(3)	C31-C32-C33	120 9(4)
C1-N6-N5	109 8(3)	C21-N26-N25	108 7(3)	C28-C33-C32	119.6(4)
C1-C8-C13	119 1(3)	C21-C28-C33	121 4(3)	C24-C34-C39	120 8(4)
C1-C8-C9	121.4(3)	C21-C28-C29	119 5(3)	C24-C34-C35	120 6(4)
C9-C8-C13	119.5(3)	C29-C28-C33	119 1(4)	C35-C34-C39	118.6(4)
C8-C9-C10	119 5(3)	C28-C29-C30	120.6(4)	C34-C35-C36	120 2(4)
C9-C10-C11	121 4(4)	C29-C30-C31	119 6(4)	C35-C36-C37	120 4(4)
C10-C11-C12	118 8(4)	C30-C31-C32	120 1(4)	C36-C37-C38	119.9(4)
C37-C38-C39	120 6(5)	C34-C39-C38	120.4(4)		

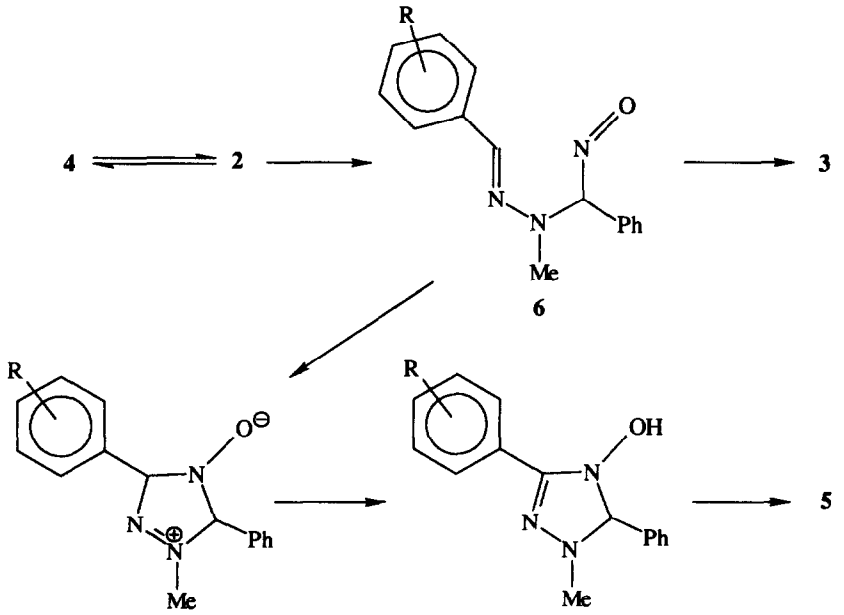
Selected torsion angles (°)

N6-C1-C8-C9	-91 6(4)	N26-C21-O22-N23	-53 1(4)
H1-C1-N6-H6	178.4(4)	C21-O22-N23-C24	18 5(4)
N3-C4-N5-N6	-1 0(5)	O22-N23-C24-N25	9 5(5)
N26-C21-C28-C29	94 0(4)	O22-N23-C24-C34	-177 4(3)
O22-C21-C28-C29	-143 0(3)	N23-C24-C34-C35	42.8(5)
N26-C21-C28-C33	-87 2(4)	N25-C24-C34-C35	-143 5(4)
O22-C21-C28-C33	35 8(5)	N25-C24-C34-C39	38 8(5)
H21-C21-N26-H26	-175 4(4)		

From the above results it seems clear that the silica gel functions as a catalyst in the transformation of the primary products of the above reactions to the corresponding triazoles. To confirm this, each of the oxatriazines **4a**, **4b** and **4e** and of the Z-hydrazoximes **2c** and **2d**, when eluted very slowly through a column of silica gel or absorbed onto the silica gel and left for several days or heated for about two hours, were completely transformed into the corresponding triazoles **5**. Under the same conditions E-hydrazoximes **3c** and **3f** remain unaltered. These results support the assigned oxime configuration and show unequivocally why the Arab authors, who don't use silica gel in their separation, don't find our triazoles in their reactions.

In agreement with current literature,[6] the addition of the methylhydrazones **1** to BNO produces the kinetically favoured Z-adduct **2**; this, under the same reaction conditions, can cyclise according to the well known rule of Baldwin, giving the ring tautomer **4**, as observed by Hussein;[2] or even irreversibly evolve towards the thermodynamically stable E-isomer **3**, as observed for the N,N-disubstituted amidoximes.[7] We have observed that when R is an electron-donor group the formation of the cyclic adduct **4** is initially favoured; in the other cases isomerisation to **3** is observed[1] instead. On contact with silica gel the above isomers exhibit different behavior and the ring-chain tautomers **4** and **2** are transformed easily into the corresponding triazoles **5**, whilst the E-isomers **3** remain, as we have already seen, unaltered. For these reasons we suggest that these transformations can occur as shown in the Scheme. It is well known that silica gel catalyses the Z/E isomerisation of amidoximes,[4] probably favouring the formation of the nitroso intermediate **6**, where the azomethine carbon becomes so nucleophilic as to give preference to the cyclisation to **5** through a facile 5-exo-trig process, only when R is an electron-repulsing group. In all other cases, when R is an electron-attracting group the cyclisation to

5 does not occur; the formation of E-isomer **3** alone takes place instead. The cyclisation to triazoles **5** of these E-isomers can be observed by acidic treatment as reported in ref. 1.



Scheme

Experimental

All melting and boiling points are uncorrected.Microanalyses were performed on a Carlo Erba EA 1102. IR spectra were recorded for Nujol mulls on a Perkin-Elmer 682 spectrometer and ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Hitachi-Perkin-Elmer R 24A (60 MHz) and on a Bruker 80 Q spectrometers, respectively, using tetramethylsilane as internal reference. Column chromatography was performed on Merck Kieselgel 70-230 mesh. Methylhydrazones **1** were prepared according to literature methods.[8] *2-Toluylaldehyde methylhydrazone* **1b**, b.p. 100-103°C at 0.8 mmHg; ν_{max}: 3359, 1600 and 1588 cm^{-1}; δ_H: 2.23(3H,s,Me), 2.72(3H,s,Me), 5.70(1H,br,NH), 6.90-7.10(3H,m,arom.), 7.52(1H,s,=CH-), 7.69-7.81(2H,m,arom.). Anal. Calcd. for $C_9H_{12}N_2$: C, 72.94; H, 8.16; N, 18.90. Found: C, 72.72; H, 8.04; N, 19.09.

Reactions of methylhydrazones **1** *with benzonitrile oxide. General Procedure.*

Benzohydroximoyl chloride (10 mmol) in chloroform (10 ml) was added dropwise to a stirred solution of methylhydrazone **1** (10 mmol) and triethylamine (30 mmol) in chloroform (40 ml) at -20°C. After stirring for 1h at room temperature, the solvent was evaporated under vacuum and the residue washed with water, dried and treated with absolute ethanol. After removal of insoluble diphenyl furoxan, the solvent was evaporated and the residue purified either by crystallisation from diethyl ether/ethanol (Method A) or by slow elution with chloroform on silica gel column (Method B).

a) *Benzaldehyde methylhydrazone* ***1a*** *and benzonitrile oxide.*

Method A. *3,6-diphenyl-4-methyl-1,2,4,5-oxatriazine* **4a** (58%), m.p. 135°;ν_{max}: 3300(sp), 1590 and 1556 cm^{-1}; δ_H : 2.87(3H, s, NMe), 4.28(1H, d, *J* 11Hz, exch.D_20, NH), 5.35 (1H, d, *J* 11Hz, C_6H), 7.25-7.70(10H,m,arom.). Anal. Calcd. for $C_{15}H_{15}N_3O$: C, 71.12; H, 5.97; N, 16.59. Found: C, 70.93; H, 5.88; N, 16.79.

Method B. *3,5-diphenyl-1-methyl-1,2,4-triazole* **5a** (55%), m.p. 80°C (lit,[9] m.p.80-82°C).

b) *2-Toluylaldehyde methylhydrazone* ***1b*** *and benzonitrile oxide.*

Method A. *4-methyl-3-phenyl-6-(2-toluyl)-1,2,4,5-oxatriazine* **4b** (53%), m.p. 132°; ν_{max}: 3295 (sp), 1588 and 1556 cm^{-1}; δ_H: 2.53(3H,s,Me), 2.90(3H, s, NMe), 4.14(1H, d, *J* 11Hz, exch.D_20, NH), 5.36(1H, *J* 11Hz, d, C_6H), 7.20-7.70(9H, m, arom.). Anal. Calcd. for $C_{16}H_{17}N_3O$: C, 71.88; H, 6.41; N, 15.72. Found: C, 72.08; H, 6.48; N, 15.99.

Method B. *1-methyl-5-phenyl-3-(2-toluyl)-1,2,4-triazole* **5b** (48%); b.p. 155-160°C at 0.4 mmHg; ν_{max}: 1630 and 1607 cm^{-1}; δ_H : 2.65(3H, s, Me), 4.00(3H, s, NMe), 7.15-8.00 (9H,m,arom.). Anal. Calcd. for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.86. Found: C, 77.29; H, 6.20; N, 17.05.

c) *Salicylaldehyde methylhydrazone* ***1c*** *and benzonitrile oxide.*

Method A. Non-separable mixture of *Salicylaldehyde (Z)-N-benzohydroxymoyl-N-methylhydrazone* **2c** and *Salicylaldehyde (E)-N-benzohydroxymoyl- N-methylhydrazone* **3c** , identified by ^1H NMR and by exposure to a column of silica gel (see Table 1).

Method B. *1-methyl-5-phenyl-3-salicyl-1,2,4-triazole* **5c** (42%); m.p. 92°;[10]ν_{max} : 1630 and 1600 cm^{-1}; δ_H : 3.97(3H, s, NMe), 6.96-8.15(9H, m, arom.), 10.97 (1H, br, 0H) and *Salicylaldehyde (E)-N-benzohydroxymoyl- N-methylhydrazone* **3c** (15%);m.p.145°; ν_{max}: 3207(br), 3109(br), 1646 and 1619 cm^{-1}; δ_H : 3.52(3H, s, Me), 6.64-7.58(9H, m, arom.), 7.61 (1H,s,=CH-), 10.05(br, 0H). Anal. Calcd. for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.61. Found: C, 66.69; H, 5.48; N, 15.83.

d) *2-methoxybenzaldehyde methylhydrazone* ***1d*** *and benzonitrile oxide.*

Method A. Non-separable mixture of *2-methoxybenzaldehyde (Z)-N-benzohydroxymoyl-N-methyl-hydrazone* **2d** and *4-methyl-3-phenyl-6-(2-methoxyphenyl)-1,2,4,5-oxatriazine* **4d**, identified by ^1H NMR and by exposure to a column of silica gel (see Table 1).

Method B. *3-(2-methoxyphenyl)-1-methyl-5-phenyl-1,2,4-triazole* **5c** (42%);[10] m.p. 105°;ν_{max} : 1610 and 1590 cm^{-1}; δ_H : 3.88(3H, s, OMe), 3.95(3H, s, NMe), 6.88-8.05(9H, m, arom.).

e) *4-methoxybenzaldehyde methylhydrazone* ***1e*** *and benzonitrile oxide.*

Method A. *6(4-methoxyphenyl)-4-methyl-3-phenyl-1,2,4,5-oxatriazine* **4e** (55%), m.p. 138°;ν_{max}: 3300(sp), 1593 and 1568 cm^{-1};δ_H : 2.87(3H, s, NMe), 3.80(3H, s, OMe), 4.22(1H, d, *J* 11Hz, NH), 5.25(1H, d, *J* 11Hz, C_6H), 6.87-7.61(9H, m, arom.). Anal. Calcd. for $C_{16}H_{17}N_3O_2$: C, 67.82; H, 6.05; N, 14.83. Found: C, 67.66; H, 5.93; N, 15.05.

Method B. *3-(4-methoxyphenyl)-1-methyl-5-phenyl-1,2,4-triazole* **5e** (49%); m.p. 117°;ν_{max} : 1620 and 1588 cm^{-1}; δ_H : 3.85(3H, s, OMe), 4.00(3H, s, NMe), 6.75-8.10(9H, m, arom.); δ_C: 36.1, 54.5,113.3, 123.4, 127.1, 127.5, 128.1, 129.2, 154.6, 159.8, 160.2. Anal. Calcd. for $C_{16}H_{15}N_3O$: C, 72.43; H, 5.70; N, 15.84. Found: C, 72.59; H, 5.98; N, 15.98.

f) *4-nitrobenzaldehyde methylhydrazone* ***1e*** *and benzonitrile oxide.*

From both methods, together with unidentified by products, was obtained the ***4-nitrobenzaldehyde (E)-N-benzohydroxymoyl-N-methylhydrazone*** **3f** (32%);[10] m.p. 154°;ν_{max} : 3185(br), 1655 and 1619 cm^{-1}; δ_H : 3.55(3H, s, NMe), 7.15-8.16(10H, m, arom.), 10.9(1H, br, 0H).

Crystal Structure Analysis for ***4a*** *– Crystal data..* $C_{15}H_{15}O_1N_3$, M_r=253.3, monoclinic, $P2_1/c$, a=9.902(2), b=27.220(3), c=9.975(2) Å, ß=90.05(2)°, V=2688.7(5) $Å^3$, Z=8, Dc=1.25 g cm^{-3}, λ (MoKα) = 0.71073 Å, μ=0.076 mm^{-1}, F(000)=1072, T=296 K, R=0.042 and Rw=0.059.

Crystals suitable for X-ray analysis were obtained by recrystallization from methanol solutions. A crystal of dimensions 0.25x0.33x0.29 mm was used for intensity-data collection at 296 K with a Siemens R3m/V four-circle diffractometer using graphite-monochromated MoKα (λ = 0.71073 Å) radiation. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 2θ, ω, χ and φ values of 25 strong reflections in the range 12<2θ<24°. Crystal and electronic stability was confirmed by the constancy of three check reflections measured for every 120 min of X-ray exposure. Of 4763 independent reflections measured by the ω/2θ scan technique, in the range 3<2θ<50 (-3 < h <11, -5 < k < 32 ,-11< l <11), 1927 (R_{int} =0.0059) having net intensity F≥ 4σ(F) were used in the solution and refinement of the structure. Corrections for Lorentz polarization effects were made, absorption correction was made using an empirical method based on ψ scans (ψ=0-360° every 10°) for χ values near 90°, (max and min transm. = 0.9773/0.9932).

Structure determination. The structure was solved by direct methods with the MULTAN 80 system[11]; subsequent calculations were mainly carried out by the SHELX76[12] and PARST[13] systems of programs on the VAX-3400 computer at the "Centro Interdipartimentale di Servizi per la Diffrattometria a Raggi-x dell'Università di Messina". All the H atoms were added at calculated positions and included in the structure factor calculation with a common thermal parameter (U=0.05 $Å^2$). The structure was anisotropically refined by the full-matrix least-squares method. The final R values were $[\sum||Fo|-|Fo||/\sum|Fo|=0.042$ and Rw $[\sum w(|Fo|-|Fc|)^2/\sum w|Fo|^2]^{1/2}=0.059$. The weighting scheme used in the last refinement cycle was $w=1.000/[\sigma^2(F_o)+0.0102\ F_o^2]$, G.O.F=0.53. Final difference map peaks were in the range 0.19, -0.19 $eÅ^{-3}$; max Δ/σ=0.024. Scattering factors for the non-hydrogen atoms were taken from ref.14 and for H atoms from ref. 15

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