

Note

Synthesis and characterization of  
N, N'-aliphatic dicarboxylbis-  
(hydrazones)

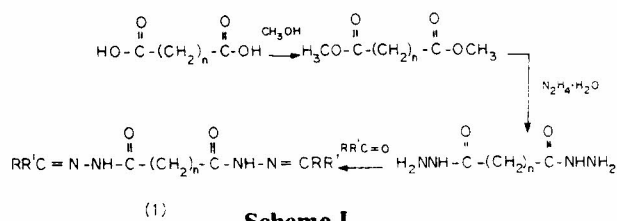
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N,N'-Malonylbis-, N,N'-adipinylbis- and N,N'-sebacoylbis-  
(hydrazones) **1** of various aldehydes and ketones have been  
prepared and characterized by elemental analyses, melting  
points, and <sup>1</sup>H NMR and IR spectral data.

Polymers containing N-N bonds have found a  
variety of applications in recent years<sup>1</sup>. Realizing the  
reactivity of N-N bonds, several N-N bonded epoxy  
resins from bis-carbono- and bis-thiocarbono- hydra-  
zones were prepared in our laboratory, specifically to  
use them as binders for powder propellant composi-  
tions<sup>2,3</sup>. Recently, a yet new series of epoxy resins  
based on N,N'- aliphatic dicarboxylbis (hydrazones)  
has been synthesised and used as energetic binders  
for solid propellants<sup>4</sup>. Besides the usage of N,N'-ali-  
phatic dicarboxylbis (hydrazones) as starting materi-  
als for the synthesis of these novel epoxy resins, they  
are found to have potential pharmacological proper-  
ties and tuberculostatic activity<sup>5,6</sup>. A survey of litera-  
ture, however, revealed that only a few compounds  
are reported and characterized properly. In view of  
this it was decided to standardise the method of  
preparation and characterize them systematically.  
The route of synthesis adopted to prepare these com-  
pounds is shown in Scheme I.



Scheme I

The dicarboxylic acids were first converted to  
their methyl esters by reacting with methanol. The  
dihydrazides of malonic, adipic, and sebacic acids  
were obtained by slowly adding 1 mole of dimethyl  
ester of the respective diacid into a 1 litre round  
bottomed flask containing 2.10 moles of hydrazine  
hydrate in 500 mL of ethyl alcohol and refluxing the  
mixture for 3 hr. The solid dihydrazide formed was  
collected and recrystallized from water. The recryst-  
tallized hydrazides of malonic, adipic and sebacic  
acids melt at 154°, 182° and 189°, respectively<sup>7</sup>. The  
bis(hydrazones) **1** of furfuraldehyde, vanillin, benz-  
aldehyde, cyclohexanone and butanone were pre-  
pared by two methods as given in Experimental  
Section.

The elemental analysis and melting points data are  
given in Table I.

An interesting property of these hydrazones is that  
most of them ignite spontaneously on coming into  
contact with nitric acid. The ignition delay as meas-  
ured using a set up developed earlier in our labora-  
tory<sup>8</sup>, shows that some of these compounds indeed  
have very short ignition delays (Table II). The igni-  
tion delay appears to increase with the increase in the  
number of methylene spacer groups. However, the  
dicarboxylbis (hydrazones) based on butanone, benz-  
aldehyde and cyclohexanone do not ignite at all.

The melting points of N,N'- sebacoylbis(furfural-  
dehydehydrazone) **1c** and N,N'- adipinylbis(vanillin-  
hydrazone) **1b** are quite different from the reported  
values. This could happen mainly if there is a mixture  
of mono and bisderivatives. The compounds reported  
by earlier workers are possibly contaminated with  
monoderivatives or other impurities. However, in the  
present case, the elemental analyses as well as spec-  
tral data of these compounds match very closely with  
the expected values, thereby, confirming their purity.

The spectral data given in Table II show that the  
N-H proton resonances of N-N'-dicarboxylbis(hy-  
drazones) appear as doublets in the region δ 9.85-  
11.50 ppm unlike those in bis-thiocarbono-  
hydrazones<sup>9</sup>, where they appear as singlets. Also, the  
CH<sub>2</sub> protons resonance of malonylbis(hydrazone) is

Table I—Melting points and elemental analysis data of N,N'-aliphatic dicarboxylbis(hydrazones) I.

Compd	n	Yield (%)	m.p. (°C) Found (Reported)	Mol. formula	Found % (Calcd)		
					C	H	N
R = CH=CH-CH=C: R=H $\begin{array}{c} \text{O} \\ \parallel \\ \text{---} \end{array}$							
1a	1	98	234 (d) [230-32 (d)] <sup>5</sup>	C <sub>13</sub> H <sub>12</sub> N <sub>4</sub> O <sub>4</sub>	54.20 (54.16)	4.18 4.16	19.28 19.44)
1b	4	98.5	235 (232-34) <sup>5</sup>	C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub>	58.15 (58.18)	5.48 5.45	16.76 16.97)
1c	8	92	172 (143-46) <sup>5</sup>	C <sub>20</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub>	61.90 (62.17)	6.73 6.70	14.32 14.51)
R = <i>p</i> -OHC <sub>6</sub> H <sub>3</sub> OCH <sub>3</sub> - <i>m</i> : R=H							
1d	1	98	215	C <sub>19</sub> H <sub>20</sub> N <sub>4</sub> O <sub>6</sub>	57.30 (57.00)	5.14 5.00	13.96 14.00)
1e	4	96	206 (287) <sup>6</sup>	C <sub>22</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub>	59.64 (59.73)	6.10 5.88	12.73 12.67)
1f	8	93	180	C <sub>26</sub> H <sub>34</sub> N <sub>4</sub> O <sub>6</sub>	62.38 (62.65)	7.00 6.80	11.14 11.25)
R = C <sub>2</sub> H <sub>5</sub> : R' = CH <sub>3</sub>							
1g	1	99	144	C <sub>11</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub>	54.91 (55.00)	8.42 8.53	23.42 23.33)
1h	4	98	138	C <sub>14</sub> H <sub>26</sub> N <sub>4</sub> O <sub>2</sub>	59.21 (59.57)	9.35 9.22	20.14 19.86)
1i	8	94	115	C <sub>18</sub> H <sub>34</sub> N <sub>4</sub> O <sub>2</sub>	63.25 (63.91)	10.08 10.06	16.48 16.57)
R = C <sub>6</sub> H <sub>5</sub> : R' = H							
1j	1	96	220	C <sub>17</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub>	66.42 (66.23)	5.23 5.19	18.15 18.18)
1k	4	98	215	C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub>	68.46 (68.57)	6.31 6.31	15.98 16.00)
R,R' = -(CH <sub>2</sub> ) <sub>5</sub> -							
1l	4	96	195	C <sub>18</sub> H <sub>30</sub> N <sub>4</sub> O <sub>2</sub>	65.10 (64.60)	9.05 8.95	16.59 16.76)
1m	8	95	142	C <sub>22</sub> H <sub>38</sub> N <sub>4</sub> O <sub>2</sub>	67.42 67.70	9.83 9.70	14.00 14.36)

found to be doublet at  $\delta$  3.55-3.85 whereas the resonances of -[CH<sub>2</sub>]- protons of adipinylbis- and sebacoylbis(hydrazones) appear as multiplets at  $\delta$  1.40-2.25 ppm. This could be due to the close proximity of these protons to the C=O groups. All other proton resonances appear in the regions as expected.

### Experimental Section

**General.** Melting points were determined in open glass capillaries and are uncorrected. The C and H elemental analyses of all the compounds, determined using Heraeus (mikro standard 8304071) Elemental

Table II — IR and  $^1\text{H}$  NMR spectral characterisation and ignition delay data of N,N'-aliphatic dicarboxylbis(hydrazones) 1.

Compd	Absorption frequency $\nu$ ( $\text{cm}^{-1}$ )/Chemical shift ( $\delta$ , ppm)	Ignition delay (min)*
1a	IR: 3200,3060 (NH), 2900 ( $\text{CH}_2$ ), 1680 (C=O), 1650 (C=N), 1240 (N-N), 760 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 3.55,3.85 (2H, $\text{CH}_2$ ), 6.60,6.85,7.80 (6H, Ar), 8.10 (2H, CH), 11.35,11.48 (2H, NH)	14
1b	IR: 3180,3120 (NH), 2920 ( $\text{CH}_2$ ), 1660 (C=O), 1620 (C=N) 1200 (N-N), 750 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 1.38, 2.10 (8H, $-\text{[CH}_2\text{]}_4-$ ), 6.65,6.90,7.75 (6H, Ar), 8.10 (2H, CH), 11.02,11.20 (2H, NH)	33
1c	IR: 3220, 3120 (NH), 2900 ( $\text{CH}_2$ ), 1670 (C=O), 1640 (C=N), 1240 (N-N), 750 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 1.40, 2.15 (16H, $-\text{[CH}_2\text{]}_8-$ ), 6.65, 6.90, 7.80 (6H, Ar), 8.08 (2H, CH), 11.05, 11.25 (2H, NH)	75
1d	IR: 3480 (OH), 3180 (NH), 2920 ( $\text{CH}_2$ ), 1650 (C=O), 1630 (C=N), 1160 (N-N), 740 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 3.75 (6H, $\text{OCH}_3$ ), 3.80,3.85 (2H, $\text{CH}_2$ ), 6.70-7.25 (6H, Ar), 7.85, 8.10 (2H, CH), 9.35 (2H, OH), 11.41 (2H, NH)	62
1e	IR: 3480 (OH), 3240.3100 (NH), 2940 ( $\text{CH}_2$ ), 1670 (C=O), 1620 (C=N), 1210 (N-N), 730 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 1.50, 2.15 (8H, $\text{CH}_2$ ), 3.78 (6H, $\text{OCH}_3$ ), 6.75-7.20 (6H, $\text{OCH}_3$ ), 6.75-7.20 (6H, Ar), 7.85, 8.05 (2H, CH), 9.30 (2H, OH), 10.95, 11.10 (2H, NH)	
1f	IR: 3440 (OH), 3230,3080 (NH), 2920 ( $\text{CH}_2$ ), 1650 (C=O), 1640 (C=N), 720 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 1.55, 2.25 (16H, $-\text{[CH}_2\text{]}_8$ ), 3.80 ( $\text{OCH}_3$ ), 6.85-7.35 (6H, Ar), 7.95,8.10 (2H, CH), 9.30 (2H, OH), 10.93, 10.05 (2H, NH)	175
1g	IR: 3180, 3040 (NH), 2920 ( $\text{CH}_2$ ), 1670 (C=O), 1620 (C=N), 1220, 1140 (N-N), 720 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 1.05, 1.88, 2.25 (16H, butanone), 3.55, 3.75 (2H, $-\text{[CH}_2\text{]}_2$ ), 10.11, 10.23 (2H, NH)	N.I
1h	IR: 3190, 3090 (NH), 2900 ( $\text{CH}_2$ ), 1660 (C=O), 1620 (C=N) 1200, 1120 (N-N), 730 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 1.05, 1.90, 2.25 (16H, butanone), 1.50 (8H, $-\text{[CH}_2\text{]}_4-$ ), 9.90 (2H, NH)	N.I
1i	IR: 3140, 3060 (NH), 2900 ( $\text{CH}_2$ ), 1660 (C=O), 1620 (C=N), 1200, 1120 (N-N), 740 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 1.05, 1.85,2.20 (16H, butanone), 1.45 (16H, $-\text{[CH}_2\text{]}_8-$ ), 9.85 (2H, NH)	N.I
1j	IR: 3180, 3030 (NH), 2920 ( $\text{CH}_2$ ), (C=O), 1640 (C=N), 1220, 1150 (N-N), 740 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 3.55, 3.80 (2H, $-\text{[CH}_2\text{]}_2-$ ), 7.24-7.85 (10H, Ar), 8.30 (2H, CH), 11.45, (2H, NH)	N.I
1k	IR: 3150 (NH), 2900 ( $\text{CH}_2$ ), 1660 (C=O), 1630 (C=N), 1220, 1140 (N-N), 740 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 1.45, 2.20 (8H, $-\text{[CH}_2\text{]}_4-$ ), 7.20-7.80 (10H, Ar), 8.30 (2H, CH), 11.38, (2H, NH)	N.I
1l	IR: 3320, 3220 (NH), 2900 ( $\text{CH}_2$ ), 1670 (C=O), 1640 (C=N), 1250, 1140 (N-N) 740 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 1.55 (8H, $-\text{[CH}_2\text{]}_4-$ ), 2.20, 2.45 (20H, $-\text{[CH}_2\text{]}_5-$ ), 10.10 (2H, NH)	N.I
1m	IR: 3280, 3160 (NH), 2900 ( $\text{CH}_2$ ), 1660 (C=O), 1640 (C=N), 1240, 1130 (N-N), 740 ( $\text{CH}_2$ ) $^1\text{H}$ NMR: 1.54 (16H, $-\text{[CH}_2\text{]}_8-$ ), 2.25,2.50 (20H, $-\text{[CH}_2\text{]}_5-$ ), 10.05 (2H, NH)	N.I

\* N.I=No ignition

Analyser, agree with the expected values. Nitrogen analyses were carried out on a Carlo Erba Elemental Analyser model 1106. IR spectra were recorded on a Perkin-Elmer 781 spectrometer in nujol. Most of the IR absorptions could be identified fairly easily.  $^1\text{H}$  NMR spectra were taken in  $\text{DMSO}-d_6$  /TMS on a Varian FT 80A NMR spectrometer.

**Synthesis of bis(hydrazones)1 : Method A.** This method was used when the boiling point of the aldehyde /ketone was above  $100^\circ\text{C}$ . The aldehyde/ketone (0.11 mole) dissolved in ethanol (100-150 mL) was taken in a round bottomed flask and to this was added an aqueous solution of the respective dihydrazide (0.05 mole). The mixture was then refluxed with

continuous stirring for 2-3 hr. The solid hydrazone which separated out during the reaction was filtered, washed with 30% aq. ethanol and dried over KOH in vacuum desiccator. The bis(hydrazones) of furfuraldehyde, benzaldehyde, vanillin and cyclohexanone were prepared by this method.

**Method B.** To synthesise bis (butanonehydrazones) 1 g-i, butanone (b.p.  $< 100^\circ\text{C}$ ) itself was used in excess as solvent medium. Finely powdered dihydrazide (0.05 mole) was refluxed in excess of butanone (75 mL) for 8-10 hr with continuous stirring. The excess butanone was distilled off to one-third volume. The hydrazone which crystallized out at room temperature was filtered, washed with ice-cold pet. ether and dried over KOH in a desiccator.

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