Reference Data

Diacyl Acid Dihydrazides

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N,N'-Diacyl acid dihydrazides were prepared by the reaction of acid dihydrazides with two equivalents of acyl chlorides. The structures of these compounds were eluci-

KEY WORDS N,N'-Diacyl acid dihydrazides ¹H NMR ¹³C NMR

dated by ¹H and ¹³C NMR spectroscopy.

INTRODUCTION

In connection with our work designed to synthesize substituted bis-1,3,4-oxadiazoles, 2, we prepared N, N'-diacyl acid dihydrazides 1a-ao, (Table 1) as potential precursors of 2 [Eqn (1)].

$$\begin{array}{c} O & O & O \\ \parallel & \parallel \\ R - CNHNHC(CH_2)_n CNHNHC - R & POCI_3 \\ \hline 1 & CH_3CN \\ \hline 2 \\ \end{array} \xrightarrow{N - N \\ CH_3CN \\ A \\ \hline 2 \\ \end{array} \xrightarrow{N - N \\ O \\ CH_2 \\ O \\ \hline 2 \\ \end{array}$$

RESULTS AND DISCUSSION

The ¹H and ¹³C NMR spectra are in agreement with the proposed structures. Table 2 presents the ¹H NMR data of compounds 1a-ao, and the ¹³C chemical shifts are fully assigned and given in Table 3.

O

RCNHNHC(CH₂), CNHNH

la-ao

The ¹H NMR spectra of N,N'-diacyl acid dihydrazides exhibited one or two peaks in the range $\delta 9.34$ -10.96 assigned to the NH protons. The ¹³C NMR spectra of compounds 1a-d showed characteristic ¹³C signals in the ranges $\delta 171.3-176.3$ and 165.1-

$$\begin{array}{c} & & & \\ \mathsf{N} \\ \mathsf{N} \\ \mathsf{N} \\ \mathsf{N} \\ \mathsf{H} \\ \mathsf{N} \\ \mathsf{H} \\ \mathsf{C} \\ \mathsf{H} \\ \mathsf{C} \\ \mathsf{L} \\ \mathsf{C} \\ \mathsf{H} \\ \mathsf{C} \\ \mathsf{C} \\ \mathsf{H} \\ \mathsf{C} \\ \mathsf{C} \\ \mathsf{R} \\ \mathsf{C} \\ \mathsf{C} \\ \mathsf{R} \\ \mathsf{C} \\ \mathsf{C} \\ \mathsf{C} \\ \mathsf{C} \\ \mathsf{R} \\ \mathsf{C} \\ \mathsf$$

CR

173.1 assigned to the carbonyl carbons C-a and C-b, respectively. The ¹³C chemical shifts of C-a in the other N,N'-diacyl acid dihydrazides le-ao were observed in the range δ 170.1–171.9. However, the chemical shifts of C-b were found to depend strongly on the nature of substituent R. When R is 2-furyl or

0

Table 1. Structures and melting points of N,N'-diacyl acid hydrazides

Ο

4		о НС–(СН ₂) _п –СNHN	о нс-						
(/ 0	u				X: 0,S			
Compound		в	M.n. (°C)	Compound		P	M. D. (%C)		
100.			W.p. (C)	140.			м.р. (С)		
1a	0	C ₆ H ₅	288-289	1u	3	2-Furyl	220-221		
b	0	4-CH₃OC ₆ H₄	323–324	v	3	2-Thienyl	271–272		
C	0	4-NO ₂ C ₆ H ₄	338–339	w	3	(CH₃)₂CH	240–241		
d	1	C₅H₅	238–239	x	4	C ₆ H₅	246–247		
8	1	4-CH ₃ OC ₆ H ₄	257-258	У	4	4-CH ₃ OC ₆ H ₄	270–271		
f	1	4-NO ₂ C ₆ H ₄	278–279	z	4	4-NO ₂ C ₆ H ₄	290-291		
g	1	2-Furyl	237–238	aa	4	2-Furyl	214-215		
ĥ	1	2-Thienyl	272–273	ab	4	2-Thienyl	227228		
i	1	CH,	250-251	ac	4	2-C10H7	280-281		
		3		ad	4	CH	256-257		
i	2	C _e H _e	211-212	ae	4	(เว่า (l))))))))))))))))))))))))))	285-286		
k	2	4-CH_OC_H	217-218	af	4	(CH_)_C	221-222		
i i	2	2-Furvl	215-216			(3/3-			
m	2	2-Thienvl	226-227	ad	8	C _o H _e	214-215		
n	2	2-C. H.	251-252	ah	8	4-CH_OC_H	235-236		
0	2	CH	248-249	ai	8	4-NO ₂ C ₂ H ₄	256-257		
p	2	(CH_)_CH	257-258	ai	8	2-Furvi	183-184		
a	2	(CH_)_C	230-231	≃, ak	8	2-Thienvl	248-249		
4	-	(0).3/30		al	8	CH	320-321		
r	3	C.H.	226-227	am	8	Thionhene-2-CH	243_244		
e	3	4-CH OC.H.	242-243	an	8	(CH_)_CH	245-244		
3	3	4.NO C H	278_279	20	8	(CH) C	179_170		
L	5	$+ 100_{2}0_{6}1_{4}$	210-213	au	0	(013/30	1/0-1/3		

^a Names of selected compounds: 1a = N,N'-dibenzoyloxalic acid dihydrazide; 1e = N,N'-bis(4-anisoyl)malonic acid dihydrazide; 1I = N,N'di(2-furoyl)succinic acid dihydrazide; 1v = N, N'-di(2-thienoyl)glutaric acid dihydrazide; 1af = N, N'-dipivaloyladipic acid dihydrazide; 1al = N, N'-diacetylsebacic acid dihydrazide.

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Table 2. ¹H NMR data for compounds 1a-ao^a

Compound No.	Chemical shifts (A)
1	10.61 (b. AH. NH) 7.99 (m. AH. gromatic) 7.54 (m. 6H. gromatic)
la h	10.51 (D, 4H, NH), 7.66 (H, 4H, aromatic), 7.54 (H, 6H, aromatic)
J.	$7.05 (d 4H J = 9.0 Hz aromatic) 3.85 (s 6H OCH_)$
с	10.53 (b, 4H, NH), 8.08 (m, 8H, aromatic)
d	10.29 (b, 4H, NH), 7.90 (m, 4H, aromatic), 7.50 (m, 6H, aromatic),
	3.28 (s, 2H, CH ₂)
e	10.21 (b, 4H, NH), 7.88 (d, 4H, J = 8.8 Hz, aromatic),
	7.00 (d, 4H, J = 8.8 Hz), 3.83 (s, 6H, OCH ₃), 3.31 (s, 2H, CH ₂)
f	10.54 (b, 4H, NH), 8.24 (m, 8H, aromatic), 3.32 (s, 2H, CH ₂)
g	10.20 (b, 4H, NH), 7.86 [dd, 2H, H-4, J(42) = 0.7 Hz, J(43) = 1.7 Hz, furyl],
	7.23 [dd, 2H, H-2, J(24) = 0.7 Hz, J(23) = 3.6 Hz, furyl],
	6.63 [dd, 2H, H-3, <i>J</i> (34) = 1.7 Hz, <i>J</i> (32) = 3.6 Hz, furyl],
	3.26 (s, 2H, CH ₂)
n	10.25 (b, 4H, NH), 7.83 (b, 4H, thienyl),
	7.10 [dd, 2H, H-3, J(34) = 3.8 Hz, J(32) = 4.7 Hz, thienyij, 2.29 (c. 2H, CH.)
;	3.20 (5, 20, 00 ₂) 9.78 (5, 40, 100) 3.14 (6, 20, 00) 3.50 (6, 60, 00)
i	10.15 (b, 4H, NH), 7.88 (m, 4H, aromatic), 7.68 (m, 6H, aromatic)
,	2.25 (s. 4H, CH _a)
k	10.00 (b, 4H, NH), 7.86 (d, 4H, $J = 8.6$ Hz, aromatic).
	7.01 (d, 4H, $J = 8.6$ Hz, aromatic),
	3.84 (s, 6H, OCH ₃), 2.50 (s, 4H, CH ₂)
1	10.02 (b, 4H, NH), 7.85 [dd, 2H, H-4, J(43) = 1.6 Hz, J(42) = 0.7 Hz, furyl],
	6.63 [dd, 2H, H-2, J(24) = 0.7 Hz, J(23) = 3.6 Hz, furyl],
	6.22 [dd, 2H, H-3, J(34) = 1.6 Hz, J(32) = 3.6 Hz],
	2.47 (s, 4H, CH ₂)
m	10.38 (b, 4H, NH), 7.92 (m, 4H, thienyl),
	7.17 [dd, 2H, H-3, J(34) = 3.8 Hz, J(32) = 4.8 Hz, thienyl],
	2.50 (S, 4H, CH ₂) 10.09 (b, 4H, NH) 7.95 (m, 14H, aromatic) 2.49 (c, 4H, CH,)
0	966 (b, 4H, NH) 2.45 (s, 4H, CH,) 1.97 (s, 6H, CH,)
D	9.49 (b, 4H, NH), 2.49 (septet, 2H, $J = 6.8$ Hz, CH).
r.	2.42 (s, 4H, CH ₂), 1.02 (d, 12H, $J = 6.8$ Hz, CH ₂)
q	9.53 (b, 4H, NH), 2.42 (s, 4H, CH ₂), 1.07 (s, 18H, CH ₃)
r	10.32 (b, 2H, NH), 9.92 (b, 2H, NH), 7.89 (m, 4H, aromatic),
	7.50 (m, 6H, aromatic), 2.31 (t, 4H, $J = 5.1$ Hz, CH ₂),
	1.80 (quintet, 2H, $J = 5.1$ Hz, CH ₂)
S	10.03 (b, 4H, NH), 7.88 (d, 4H, J = 8.8 Hz, aromatic),
	7.02 (d, 4H, $J = 8.8$ Hz, aromatic), 3.82 (s, 6H, OCH ₃),
	2.28 (t, 4H, $J = 6.2$ Hz, CH_2), 1.81 (quintet, 2H, $J = 6.2$ Hz, CH_2) 10.11 (b, 4H, NH), 8.22 (m, 9H, comparis), 2.27 (a, 4H, $J = 5.4$ Hz, CH_2)
t	1.85 (quintet 2H $J=5.4$ Hz CH)
	9.96 (b AH NH) 7.88 [dd 2H H-4 $I(43) = 1.6$ Hz $I(42) = 0.6$ Hz furvi]
ŭ	7.22 [dd, 2H, H-2, J(24) = 0.6 Hz, J(23) = 3.5 Hz, furyl].
	6.65 [dd, 2H, H-3, J(34) = 1.6 Hz, J(32) = 3.5 Hz, furvi],
	2.31 (t, 4H, J = 6.3 Hz, CH ₂), 1.85 (quintet, 2H, J = 6.3 Hz, CH ₂)
v	10.12 (b, 4H, NH), 7.84 (m, 4H, thienyl),
	7.19 [dd, 2H, H-3, J(34) = 3.8 Hz, J(32) = 4.9 Hz, thienyl],
	2.37 (t, 4H, J = 7.9 Hz, CH ₂), 1.86 (quintet, 2H, J = 7.9 Hz)
w	9.56 (b, 4H, NH), 2.46 (septet, 2H, J = 6.6 Hz, CH),
	2.16 (t, 4H, $J = 5.5$ Hz, CH ₂), 1.75 (quintet, 2H, $J = 5.5$ Hz, CH ₂),
	1.04 (d, 12H, $J = 6.6$ Hz, CH ₃)
x	10.09 (D, 4H, NH), 7.88 (m, 4H, aromatic), 7.51 (m, 6H, aromatic),
	2.24 (III, 4H, UH_2), 1.04 (III, 4H, UH_2) 0.06 (b. 4U, NH) 7.97 (d. 4U, $I = 9.9$ Hz, aromatic)
y	3.30 (μ, μπ, μπ), 7.07 (μ, μπ, σ ~ 0.0 π2, aromatic), 7.02 (d. ΔH. J = 8.8 Hz, aromatic), 3.82 (e. 6H, ΩCH,)
	2.22 (m, 4H, $O = 0.0$ Hz, aromatic, 3.02 (s, 0H, OOH_3), 2.22 (m, 4H, OH_2), 1.62 (m, 4H, OH_2)
	(,,

Reference Data

Table 2 (continued)

Compound	
No.	Chemical shifts (δ)
z	10.33 (b, 4H, NH), 8.22 (m, 8H, aromatic), 2.23 (m, 4H, CH ₂),
	1.64 (m, 4H, CH ₂)
aa	9.97 (b, 4H, NH), 7.88 [dd, 2H, H-4, J(42) = 0.7 Hz, J(43) = 1.7 Hz, furyl],
	7.20 [dd, 2H, H-2, J(24) = 0.7 Hz, J(23) = 3.5 Hz, furyl],
	6.64 [dd, 2H, H-3, J(34) = 1.7 Hz, J(32) = 3.5 Hz, furyl],
	2.20 (m, 4H, CH ₂), 1.65 (m, 4H, CH ₂)
ab	10.00 (b, 4H, NH), 7.83 [d, 4H(H-2,H-4), <i>J</i> (23) = 4.6 Hz, thienyl],
	7.18 [dd, 2H, H-3, $J(34) = 4.0$ Hz, $J(23) = 4.6$ Hz, thienyl],
	2.21 (m, 4H, CH ₂), 1.61 (m, 4H, CH ₂)
ac	10.20 (b, 4H, NH), 8.07 (m, 14H, aromatic), 2.57 (m, 4H, CH_2), 1.78 (m, 4H, CH_2)
ad	9.64 (b, 4H, NH), 2.11 (m, 4H, CH ₂), 1.83 (s, 6H, CH ₃), 1.51 (m, 4H, CH ₂)
ae	9.68 (b, 4H, NH), 2.26 (m, 6H, CH and CH_2), 2.11 (m, 4H, CH_2),
-	1.02 (d, 12H, $J = 6.8$ Hz, CH ₃)
af	9.38 (b, 4H, NH), 2.11 (m, 4H, CH ₂), 1.53 (m, 4H, CH ₂),
	1.13 (s, 18H, CH_3)
ag	10.02 (D, 4H, NH), 7.87 (m, 4H, aromatic), 7.51 (m, 6H, aromatic),
- h-	2.19 (m, 4H, CH_2), 1.52 (m, 12H, CH_2) 0.84 (h. 411, N11), 7.85 (d. 411, (-9.7 k), cromotic), 7.01 (d. 411, (-9.7 k), cromotic)
an	9.64 (0, 4H, NH), 7.85 (0, 4H, $J = 8.7$ Hz, aromatic), 7.01 (0, 4H, $J = 8.7$ Hz, aromatic), 2.81 (6, 6H, OCH), 2.14 (m, 4H, CH), 1.48 (m, 12H, CH))
-!	3.61 (S, OH, UCH ₃), 2.14 (M, 4H, CH ₂), 1.46 (M, 12H, CH ₂) 10.09 (h, 4H, NH), $\overline{3}$ OE (m, 9H, arometic), 2.17 (m, 4H, CH ₂)
aı	1.009 (0, 4H, NH), 7.95 (III, 6H, aromatic), 2.17 (III, 4H, CH ₂),
ai	1.45 (II), 12D, CD_2) 0.90 (b, ALL NL), 7.97 (b, 2Ll fund), 7.20 [d, 2Ll L, 2, $I(22) = 2.2$ L, fund]
aj	6.63 [dd 20 H 3 $I/(24) = 1.5$ Hz $I/(22) = 2.2$ Hz fund]
	2.16 (m 14 CH) 1.51 (m 124 CH)
ak	10.03 (b) 4H NH 7.82 [d) 4H 1/23 = 4.2 Hz this null
an	7.17 [dd 2H H-3 /(34) = /(32) = 4.2 Hz thienvil
	$2.18 \text{ (m } 4H \text{ CH}_{-}) 1.46 \text{ (m } 12H \text{ CH}_{-})$
al	9.63 (b, 4H, NH), 2.15 (m, 4H, CH _a), 1.83 (s, 6H, CH _a), 1.35 (m, 12H, CH _a)
am	9.88 (b, 4H, NH), 7.36 (m, 2H, thienvi), 6.95 (m, 4H, thienvi).
	3.68 (s. 4H, CH ₂), 2.11 (m. 4H, CH ₂), 1.39 (m. 12H, CH ₂)
an	9.57 (b, 4H, NH), 2.47 (m, 2H, CH), 2.19 (m, 4H, CH ₂), 1.36 (m, 12H, CH ₂),
	1.03 (d, 12H, $J = 6.7$ Hz, CH ₂)
ao	9.34 (b, 4H, NH), 2.12 (m, 4H, CH ₂), 1.36 (m, 12H, CH ₂), 1.09 (s, 18H, CH ₃)
^a All spectra	were recorded in DMSO-d ₆ .

Table 3. ¹³C NMR data for compounds 1a-ao^a

			Aromatic carbons					Heteroaromatic carbons			Methylene	
Compound	C-a	C-b	C-1	C-2	C-3	C-4	C-1	C-2	C-3	C-4	carbons	Other carbons
1a	175.2	173.1	131.5	129.7	127.5	133.3						
b	173.6	171.9	129.1	125.5	112.3	161.9						54.5 (OCH ₃)
с	176.3	174.3	139.3	129.5	123.8	149.9						
d	171.3	165.1	131.6	128.2	127.3	132.1					39.9	
8	170.2	164.0	129.2	124.5	113.5	161.9					39.5	55.2 (OCH ₃)
f	171.6	166.6	138.6	129.1	123.3	149.7					39.8	
g	170.9	157.1					146.7	114.3	111.5	145.3	39.8	
h	171.2	160.9					140.0	130.9	125.5	128.8	39.8	
i	171.8	173.5									39.7	14.6 (CH ₃)
j	171.2	164.8	131.5	128.5	127.4	132.8					28.4	
k	171.3	163.6	129.0	124.6	113.5	161.8					28.4	55.2 (OCH ₃)
I	171.2	157.0					145.1	114.1	111.3	145.1	28.3	
m	170.9	160.3					137.2	131.3	127.5	128.7	28.4	
n	171.3	164.3	124-134 (naphthyl carbons)							28.8		
ο	171.5	173.0									28.3	14.2 (CH ₃)

Reference Data

Methylene Heteroaromatic carbons Aromatic carbons C-4 Other carbons Compound C-a C-b C-1 C-2 C-3 C-4 C-1 C-2 C-3 carbons 171.0 174.4 28.5 31.3 (CH), 18.3 (CH₃) p 170.9 174.1 28.5 37.3 (C), 19.7 (CH₃) q 32.5, 21.0 171.0 165.6 131.4 128.2 127.2 132.5 r 170.0 165.2 129.1 124.6 113.5 161.5 32.4, 21.0 55.2 (OCH₃) s t 171.9 165.8 138.5 128.6 123.6 149.2 32.5. 21.1 32.6, 21.0 170.8 157.1 145.9 114.4 111.2 145.3 u 160.0 131.2 124.7 128.7 32.4, 20.9 v 171.0 137.4 171.4 175.4 32.5, 21.0 31.6 (CH), 18.9 (CH₃) w 127.2 132.5 32.9. 24.5 171.1 165.3 131.3 128.1 х 164.8 129.0 124.8 113.4 161.7 33.0, 24.5 55.1 (OCH₃) 171.1 v 166.6 32.9, 24.4 170.9 138.3 128.7 123.0 149.1 z 171.4 156.9 146.2 114.0 111.4 145.2 32.8. 24.4 aa 171.2 160.4 137.1 131.0 124.7 128.8 32.9, 24.4 ab ac 171.0 165.5 125-135 (naphthyl carbons) 32.7, 24.5 170.9 174.9 32.9, 24.5 21.2 (CH₃) ad 329 245 32.0 (CH), 19.3 (CH₃) 170.8 174.9 ae 32.8, 24.5 37.8 (C), 19.6 (CH₃) af 171.6 174.0 33.1, 28.3, 24.8 ag 171.3 165.5 131.7 1281 127.3 132.5 ah 171.1 168.9 128.9 124.8 113.7 161.7 33.2, 28.5, 24.7 55.2 (OCH₃) 148.8 33.0. 28.5. 24.8 171.4 166.7 138.4 128.9 123.0 ai 171.3 156.7 146.5 114.3 111.5 145.4 33.2, 28.4, 24.3 aj 131.0 124.7 128.8 33.1, 28.3, 24.6 171.4 160.3 137.1 ak 171.1 174.0 33.3, 28.5, 24.4 21.0 (CH₃) al 170.3 174.7 135.1 127.7 125.5 126.3 33.4, 28.5, 24.4 39.3 (CH₂) am 170.1 174.7 33.4, 28.4, 24.4 32.2 (CH), 19.5 (CH₃) an 171.1 174.6 33.4, 28.5, 24.4 37.7 (C), 19.7 (CH₃) ao ^a All spectra were recorded in DMSO-d₆.

2-thienyl, C-b absorbs in the range $\delta 157-160$. In the case of phenyl, substituted phenyl or naphthyl, a downfield shift was observed for the C-b chemical shift and it appeared in the range $\delta 163.6-166.6$. A further downfield shift for the C-b signal occurred in the case of alkyl substituents, where it resonated in the range $\delta 173.5-175.5$.

EXPERIMENTAL

 Table 3 (continued)

Melting points were measured on an electrothermal digital melting point apparatus. The ¹³C NMR spectra were recorded in the PFT mode at ambient temperature with internal deuterium lock using a Bruker WP 80-SY spectrometer (20 MHz). The pulse duration was 3 μ s and the sweep width was 4500 Hz. The ¹H NMR spectra were recorded on a Bruker WP 80-SY spectrometer (80 MHz). The pulse duration was 1 μ s and the sweep width was 800–1050 Hz. All chemical shifts were determined on the δ scale (ppm) relative to internal tetramethylsilane. Chemicals were purchased from Aldrich and were used without further purification.

Acid dihydrazides were prepared from the reactions of the corresponding diacid esters with hydrazine hydrate following a literature procedure.² All elemental analyses were satisfactory.

Preparation of N, N'-diacyl acid dihydrazides 1a-ao

To a stirred solution of the appropriate acid dihydrazide (25 mmol) and sodium carbonate (50 mmol) in tetrahydrofuran (50 ml) and water (50 ml), a solution of acyl chloride (50 mmol) in tetrahydrofuran (20 ml) was added dropwise. The reaction mixture was stirred at ambient temperature for 1 h. A heavy precipitate was formed which was collected by filtration, washed with water and dried. Recrystallization from dimethyl sulphoxidewater (1:1) gave colourless crystalline products, **1a-ao**.

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