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Preparation of t-Morpholinones and Their Biological Activities

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In connection with elucidating the role of L-leucine as a neuroactive substance, the authors prepared 2-morpholinones by a ring closure from carboxyl group and amino group of L-leucine with alkylene oxide. These compounds were tested as to the pesticidal activity. Only 2-cyclohexylamino-1-phenyl-ethanol had the activity against adults of *Tetranychus cinabarius*.

INTRODUCTION

There are many reports on the synthesis of 2-morpholinone. Namely, Knorr (1899) prepared 4-methyl-2-morpholinone (I) by heating ethylene oxide with sarcosine, followed by removal of water from the intermediate N-ethanolamino acid.

The method has been applied successfully by Kiprianov

et al. (1953)

2-methylamino-ethanol
at

4-(2-

3,3-diphenyl-4-methyl-2-morpholinone

De Mouilpied (1905) synthesized the lactone (IV), by condensing ethyl phenylglycinoacetate with benzaldehyde in benzene solution, in the presence of theoretical amounts of sodium ethoxide. Cocker (1943) prepared N-benzenesulphonyl-6-methyl-2-morpholinone by treating LD-N-hydroxypropylglycine in alkaline solution with benzenesulphonyl chloride.

An interesting method involving dicarboxymethylation leads to 4-carboxymethyl-2-morpholinone (Ziemlak *et al.*, 1950). At first, ethanolamine was treated with a mixture of sodium cyanide and formaldehyde in alkaline solution. Then, by rendering the reaction product to acid, 4-carboxymethyl-2-morpholinone (V) was obtained.

Pascal (1957) synthesized N-(2-hydroxyethyl)-3-isobutyl-2-morpholinone by applying Kiprianov's method from L-leucine and ethylene oxide. Jankowski *et al.* (1963) also reported some derivatives of N-substituted 2-morpholinone but the yield of the synthesized compounds was quite very low. More recently, Vieles and Galsomias (1967) prepared 2-morpholinium salts by the reaction of ethyl 2-chloropropionate with tertiary aminoalcohols and discussed about their optical properties.

Present paper deals with syntheses of some derivatives of 2-morpholinone by using propylene oxide and styrene oxide as the combining moiety. These compounds were tested as to the insecticidal activity.

SYNTHESES

General procedure

Epoxides (0.1 mole) was heated with the appropriate amines (0.1 mole) in an autoclave at 150°C for 6 hours. The resulting aminoalcohols were distilled *in vacuo* in order to remove tertiary aminoalcohols produced as by-product.

Then aminoalcohols were heated under reflux with ethyl chloroacetate (0.1 mole) for 4-5 hours in an oil bath.

The reaction mixture was then cooled, alkalified with aq. Na_2CO_3 solution and extracted with CHCl_3 3 times. The dried (Na_2SO_4) CHCl_3 extract was distilled. When necessary, crude lactones were purified by picrate formation.

Preparation of aminoalcohols

(1) By the reaction of primary amines and propylene oxide or 1,2-butylene oxide, several aminoalcohols were prepared as the combining moiety.

(2) Reaction of styrene oxide and a series of primary amines. Results are summarized in Table 1.

After distillation *in vacuo*, the distillate crystallized mostly. Recrystallization was carried out from n-hexane. Nos. 8 and 9 were recrystallized from n-hexane : acetone (2 : 1).

Preparation of 2-morpholinones

Each of alkylene oxide and styrene oxide (0.1 mole) was treated with aliphatic, aromatic or alicyclic primary amines (0.1 mole) at 150°C for 5-6 hours. Condensed products were purified by means of fractional distillation *in vacuo*.

(1) Preparation of N-substituted-6-methyl-2-morpholinones

A typical method adopted was shown in an example of 4-ethyl-6-methyl-2-morpholinone (Cahill et al., 1969).

4-Ethyl-6-methyl-2-morpholinone

2-Ethylamino-1-methyl-ethanol (4.6 g) was heated with ethyl chloroacetate (12.2 g) in an oil bath (150°C) for 4 hours, then the mixture was cooled, alkalified with aq. Na_2CO_3 solution and extracted 3 times with CHCl_3 . The dried CHCl_3 extract was evaporated and the residue was distilled to give No. 12.

4,6-Dimethyl-2-morpholinone (No. 11)

Sarcosine (0.1 mole) was mixed with Na_2CO_3 (0.4 mole), allowed to stand with propylene oxide (0.1 mole) for several hours, then the mixture was neutralized with conc. HCl to pH 6, concentrated on a water bath, and distilled *in vacuo*. A fraction of b. p. $95^\circ\text{C}/17\text{ mmHg}$ was collected (Pascal, 1957). The result-

Table 1. Reaction of styrene oxide and primary amines.

No.	R	m. p. °C or b. p. (°C/mmHg)	Yield (%)	Elemental Analysis (Found/Calcd.)			
				C	H	N	Ref.
1	—CH ₂ CH ₃	80-1	24.2				Emerson (1945)
2	—CH ₂ CH ₂ CH ₃	(115—6/0.25)	11.1	73.35 73.70	9.15 9.56	7.54 7.81	
3	—CH $\begin{smallmatrix} \text{CH} \\ \text{CH}_3 \end{smallmatrix}$	88-9.5	41.1				Emerson (1945)
4	—CH ₂ CH ₂ CH ₂ CH ₃	56-7	28.9				Kanao (1930)
5	—CH ₂ CH $\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$	58-9	25.8				„
6	—CH $\begin{smallmatrix} \text{CH}_2\text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$	(110/0.1)	44.5	73.72 74.57	9.77 9.91	7.11 7.25	
7	—C(CH ₃) ₂ —CH ₃	88-9	40.4	74.43 74.57	9.98 9.91	7.23 7.25	
8	—	(163—8/0.2)	52.1				Brown <i>et al.</i> (1952)
9	—CH ₂ —	99-100	30.8	79.07 79.26	7.49 7.54	6.08 6.16	
10	—	89-90	34.0	76.81 77.06	9.64 9.18	6.29 6.42	

ing compound was identified by hydroxamic acid test and thin layer chromatography. As spray reagent in TLC Dragendorff's reagent and ninhydrin were used.

Results obtained on other samples are shown in Table 2.

(2) Preparation of *N*-substituted-6-ethyl-2-morpholinones

These compounds were prepared by the similar method as described above (No. 12), using aminoalcohols obtained from 1,2-butylene oxide and amines. Results are given in Table 3.

(3) Preparation of *N*-substituted-6-ethyl-2-morpholinones

These compounds were also synthesized by the similar procedure mentioned above using 1-arylaminoalcohols obtained from styrene oxide and amines. Results are shown in Table 4.

Table 2. 2-Morpholinones obtained from aminoalcohols and ethyl chloroacetate.

No.	R	b. p. °C/mmHg or m. p.(°C)	Yield (%)	m. p. Picrate (°C)	Elemental Analysis (Found/Calcd.)			
					C	H	N	Ref.
11	—CH ₃	95/17						Pascal (1957)
12	—CH ₂ CH ₃	90—2/0.7	29.7	156-7.5	41.88 41.90	4.32 4.56	14.94 15.05	
13	—CH $\begin{smallmatrix} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{smallmatrix}$	97—106/2.5	30.3	124—5				Cahill <i>et al.</i> (1969)
14	—CH ₂ CH ₂ CH ₂ CH ₃	98—103/0.8	25.5	160-2	45.02 45.00	5.01 5.04	13.81 14.00	
15	—CH ₂ CH $\begin{smallmatrix} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{smallmatrix}$	109—111/0.5	47.8	183-5	44.89 45.00	5.06 5.04	13.94 14.00	
16	—CH $\begin{smallmatrix} \diagup \text{CH}_2\text{CH}_3 \\ \diagdown \text{CH}_3 \end{smallmatrix}$	98—109/0.5	37.3	132-3	44.95 45.00	5.03 5.04	13.88 14.00	
17	—C(CH ₃) ₂ —CH ₃	94—5/2	29.4					Cahill <i>et al.</i> (1969)
18		(67—9)	21.3	—				„
19	—CH ₂	154—5/1	38.4	—				„
20		131—4/0.3	30.7	191-3				„

(4) The reaction of L-leucine ethylester with several epoxides

Some new 2-morpholinones were synthesized by the condensation of propylene oxide or 1,2-butylene oxide with leucine ethylester.

4-(2-hydroxyethyl)-3-isobutyl-2-morpholinone (No. 41)

From L-leucine ethylester and ethylene oxide, this compound was prepared according to Pascal's report (1957).

Table 3. 2-Morpholinones obtained from l-ethylaminoalcohols and ethyl chloroacetate.

No.	R	b. p. °C/mmHg	Yield (%)	m. p. Picrate (°C)	Elemental Analysis (Found/Calcd.)		
					C	H	N
21	—CH ₂ CH ₃	105—9/0.1	20.4	156—8	43.80 43.52	4.83 4.70	14.20 14.50
22	—CH ₂ CH ₂ CH ₃	102—5/0.7	35.9	120—1	45.25 45.00	5.07 5.04	14.05 14.00
23	—CH $\begin{matrix} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{matrix}$	155—60/0.15	35.9	163—5	45.18 45.00	5.09 5.04	13.59 14.00
21	—CH ₂ CH ₂ CH ₂ CH ₃	105—10/0.7	20.4	129—30	45.67 46.37	5.16 5.35	13.38 13.52
25	—CH—CH $\begin{matrix} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{matrix}$	96—9/0.2	43.6		63.56 64.83	10.19 10.34	7.67 7.56
26	—CH $\begin{matrix} \diagup \text{CH}_2\text{CH}_3 \\ \diagdown \text{CH}_3 \end{matrix}$	105—11/0.2	46.3		63.58 64.83	10.23 10.34	7.64 7.56
27	—C(CH ₃) ₂ —CH ₃	100—3/0.8	36.5	180—3	45.95 46.37	5.22 5.35	13.65 13.52
28	—CH ₂ —	165—5/0.4	25.1		—	—	—
29	—CH ₂ —	156—9/0.15	45.3		69.48 71.20	8.17 7.82	6.41 6.39
30	—	151—3/0.5	37.4		48.92 49.09	5.48 5.49	12.59 12.72

Acetylation of 4-(2-hydroxyethyl)-3-isobutyl-2-morpholinone (No. 42)

4-(2-Hydroxyethyl)-3-isobutyl-2-morpholinone was refluxed with anhydrous acetic acid on an oil bath for **30** minutes. After being cooled, the mixture was washed with cold water, and extracted with CHCl₃. Then, the extract was distilled *in vacuo* to give No. **42**.

4-(2-Hydroxypropyl)-3-isobutyl-6-methyl-2-morpholinone (No. 43)

L-Leucine ethylester hydrochloride (0.01 mole) was treated with EtONa, then mixed with propylene oxide (0.02 mole) and heated at 100°C in an autoclave for 24 hours. After cooled, the solvent was evaporated, and the residue was passed down in silica gel column with CHCl₃ to give No. 43.

Table 4. 2-Morpholinones obtained from 1-arylaminoalcohols and ethyl chloroacetate.

No.	R	b. p. °C/mmHg	yield (%)	m. p. Picrate (°C)	Elemental Analysis (Found/Calcd.)			
					C	H	N	Ref.
31	—CH ₂ CH ₃	150—3/0.2	16.0	180—2	49.45 49.77	4.14 4.18	12.85 12.90	
32	—CH ₂ CH ₂ CH ₃	155/0.4	40.9	178—9	50.10 50.89	4.50 4.50	12.43 12.50	
33	—CH<CH ₃ CH ₃	155/0.2	32.7	191—2	50.60 50.89	4.51 4.50	12.34 12.50	
34	—CH ₂ CH ₂ CH ₂ CH ₃	164/0.5	33.5	—	—	—	5.51 6.00	
35	—CH ₂ CH<CH ₃ CH ₃	154—6/0.5	38.3	161—2	51.88 51.95	4.87 4.80	11.77 12.12	
36	—CH<CH ₂ CH ₃ CH ₃	153/0.3	46.6	169—70	52.13 51.95	4.85 4.80	11.87 12.12	
37	—C<CH ₃ CH ₃	—	—	—	51.82 51.95	4.82 4.80	11.92 12.12	
38	—	71—91/0.2	84.6	—	—	—	—	Janko- wski et al. (1968)
39	—CH ₂ -	210/0.9	60.2	—	55.02 55.64	4.05 4.06	11.08 11.29	
40	—	192—4/0.2	56.4	—	—	—	—	

6-Ethyl-4-(2-hydroxybutyl)-3-isobutyl-2-morpholinone (No. 44)

L-Leucine ethylester hydrochloride (0.01 mole) was treated with EtONa, then mixed with 1,2-butylene oxide (0.02 mole) and heated at 100°C in an autoclave for 24 hours. After cooled, the reaction mixture was fractionally distilled *in vacuo* to give No. 44.

6-Phenyl-3-isobutyl-2-morpholinone (No. 45)

L-Leucine ethylester hydrochloride (0.01 mole) was treated with EtONa, then mixed with styrene oxide (0.01 mole) and heated at 100°C in an autoclave for 24 hours. After cooled, a white crystalline N-(2-phenyl-2-hydroxyethyl)-L-leucine (No. 46) was obtained. 231–233°C (decomp.), yield 0.2g (9.0 %). The filtrate separated from crystals was distilled *in vacuo* to give No. 45.

These results are shown in Table 5.

Table 5. 2-Morpholinones obtained from leucine ethylester.

No.	Structure	b. p. °C/mmHg or m. p.(°C)	Yield (%)	Analysis (Found/Calcd.)			
				C	H	N	Ref.
41		183–6/6	70.0				Pascal (1957)
42		146–8/3	55.0	57.42 59.24	8.56 8.70	5.22 5.76	
43			8.5			5.76 6.11	
44		150/0.7	31.2	63.22 64.82	10.32 11.27	5.26 5.40	
45		148–50/0.5	22.4			4.23 5.40	
46		(231–3)	9.0	66.77 66.90	8.49 8.42	5.64 5.57	

(5) Condensed ring systems of 2-morpholinone

Following condensed ring compounds of 2-morpholinone and their starting moieties were prepared by the method described by Cahill et al. (1969).

4-Benzoyl-2-morpholinone (No. 50).

Monochloroacetic acid (0.11 mole) and aq. 30 % NaOH 0.22 mole were added slowly at the same time to ethanolamine (0.1 mole) maintaining at 70–80°C. The mixture was stirred for 3 hours, and diluted with water to give a 10–20 % solution. After cooled, benzoyl chloride (0.08 mole) was added dropwise to the solution at room temperature, and the pH of the reaction mixture was kept at 9–11 by addition of aq. NaOH. The mixture was further stirred for 3 hours at room temperature, then acidified to pH 3. The product obtained was washed with water and aq. NaOH until neutral. White crystalline product was obtained.

N-(2-Hydroxyethyl)-N-carboxymethylglycine (No. 51)

A mixture of ethanolamine (0.3 mole), monochloroacetic acid (0.3 mole) was stirred for 3 hours at 85°C, then cooled, and finally evaporated *in vacuo* to obtain white crystalline residue. It was recrystallized from H₂O-EtOH.

4-Carboxymethyl-5-isobutyl-2-morpholinone (No. 52)

L-Leucinol (0.1 mole) was refluxed for 4 hours with ethyl chloroacetate (0.1 mole). Then the mixture was cooled, alkalinized with aq. Na₂CO₃ and extracted 3 times with CHCl₃. The dried CHCl₃ extract was evaporated to remain No. 52. The product was purified by distillation.

These results are illustrated in Table 6.

Table 6. Condensed ring compounds of 2-morpholinones.

No.	Structure	m. p. °C or b. p. (°C/mmHg)	Yield (%)	Analysis (Found/Calcd.)			
				C	H	N	Ref.
47		66-7 (153-65/0.8)	34.9				Cahill et al. (1969)
48		91-2 (137-40/0.2)	25.0				
49		62 -3	20.0				
50		99-100 picrate 165-8	12.2	43.65	5.48	16.98 16.96	
51		180-3(dec.)	82.0	40.36 40.68	6.37 6.26	7.75 7.91	
52		(150-5/0.6)	9.0				

Chemical and optical properties of some aminoalcohols and 2-morpholinones**(1) Infrared spectrometry**

2-Morpholinones have two characteristic absorption bands, C=O stretching vibration and C-O stretching one (1150 cm⁻¹). The intense C=O stretching vibration occurs at higher frequencies than that of normal ketones. The carbonyl

Fig. 1. IR Spectrum of 6-Ethyl-4-isobutyl-2-morpholinone.

Fig. 2. NMR Spectrum of α -[(Isobutylamino) methyl] benzyl alcohol.

Fig. 3. NMR Spectra of α -[(Benzylamino) methyl] benzyl alcohol.

absorption of 6-ethyl-4-isobutyl-2-morpholinone occurred at 1740cm^{-1} as shown in Figure 1.

(2) NMR spectrometry

The NMR spectra were determined on a 60MHz and a 100 MHz spectrometer as 10 % solution in CCl_4 , with TMS as internal reference.

The NMR spectrum of 2-isobutyl-1-phenyl aminoalcohol provides almost conclusive conformation for the above structure. Namely, in reaction of styrene oxide with amines, it may produce the isomeric formula of which the phenyl group linked at the β -position of reaction product. However, as shown in Figure 2, the NMR spectrum showed that the reaction mechanism of styrene oxide seems to be $\text{S}_{\text{N}}2$ mechanism. In general it is well known that when the epoxides is cleaved, the hydroxyl group is attached to the carbon having rare protons. The five protons at δ 7.22 are the five benzene-ring protons. The doublet of six protons at δ 0.62, 0.93 represents the iso-propyl group. The sharp unsplit peak at δ 2.08 is the proton of hydroxyl group.

In Figure 3, ten protons at δ 7.20 are attributable to two benzene groups. The quartet around δ 4.60 is the proton attached to α -carbon. The sharp unsplit peak at δ 3.67 represents the methylene protons of benzyl group. The proton of hydroxyl group and secondary amine are investigated by D_2O exchange (B). Thus, it seems to be in δ 2.60-2.80 region, because the integration shows that the protons of δ 2.70 region are four, but as shown in Figure 3, they are varied to two protons by D_2O exchange.

(3) Mass spectrometry

The Mass spectra were determined at 75eV on an JEOL OISG instrument with source temperature 161°C .

Fig. 4. Mass Spectrum of 6-Ethyl-4-propyl-2-morpholinone.

Fig. 5. Mass Spectrum of 4-Acetoxyethyl-3-isobutyl-2-morpholinone.

PHYSIOLOGICAL ACTIVITIES OF 2-MORPHOLINONE

Moscher *et al.* (1953) reported that 3,3-diphenyl-4-methyl-2-morpholinone showed no appreciable analgesic activity below toxic doses (200 mg/Kg) and was inactive as an antihistaminic agent, sympatholytic and anticonvulsant. Izumi (1954) tested inhibitory activity of some N-bis(2-chloroethyl)-derivatives of certain amino acids against Yoshida Sarcoma. MeCHRCOOH ($\text{R}=\text{alkyl}$) was the

most active compound among tested compounds as judged by response of tumor cells and prolongation of life in tumor-burdened rats, but 2-morpholinones showed no activities. According to Lee *et al.* (1963), the morpholinone derivative (VI)

did not exhibit significant antitumor activity against Walker 256 Sarcoma, Sarcoma 180, Adenocarcinoma 755, and Leukemia L-1210. Zikmund (1960) tested the hypoglycemic activity on N-tosylated derivatives of 2-morpholinone. Cignarella *et al.* (1962) synthesized N-benzyl-2,6-dimethyl-derivative as an antiadrenergic substance. Budensky *et al.* (1964) also synthesized 4-(*p*-tolylsulfonyl)-2-morpholinone as oral antidiabetics and reported the blood sugar lowering activity and weak toxicity. More recently, Irwin *et al.* (1972) tested the anticonvulsant activity of cyclic derivatives of 2-cyclohexylamino-1-phenylethanol, but derivatives of 2-morpholinone showed low activity. Up to date, there is no report on anticholinesterase activity or insecticidal activity,

The authors tested the effect of aminoacohols and 2-morpholinones against some noxious insects.

Method of screening and tested insects

Tetranychus cinabarius (Adults) (No. 1)

After spraying on the leaf, the mortality after 24 or 48 hours was observed.

Tetranychus cinabarius (Eggs) (No. 1b)

After laying eggs, chemicals were sprayed on leaf in 24 hours, the number of hatching larvae after 7 days was counted.

Macrosiphon pusi (Adults) (No. 2)

After spraying on the insect bodies or leaf, the mortality of adults and larvae after 48 hours was observed.

Nephottettix apicalis cincticeps (Adults) (No. 3)

Spraying on the leaf, the number of fallen insects after 24, 48 and 72 hours was counted.

Prodenia litura (Larvae) (No. 4)

Leaf dip, observation of the mortality after 48 and 72 hours.

Bombyx mori (Larvae) (No. 5)

Leaf dip, observation of the mortality after 48 hours.

Meloidogyne incognita acrita (No. 6)

Soil drench and leaf spray, observation of the goal index of root systems after one month.

Musca domestica (Adults) (No. 7)

Application of the poisoned feed on a filter paper, observation of the mortality, number of unflying insects and laying eggs after **24** and **48** hours.

Periplaneta americana (Larvae) (No. 8)

Applying on the filter paper, the mortality after 48 hours was observed.

Results and discussion

The samples were dissolved in a small amount of N,N-dimethylformamide, and diluted with distilled water or acetone to make **2000** and 500 ppm aq. solution. Then diluted solutions were applied to the host plant, soils and insects. The results are summarized in Tables 7 and 8.

Some compounds substituted with n-butyl, isobutyl, cyclohexyl had the insecticidal activity to a certain extent. These compounds, however, brought about the plant injury too. On the other hand, **Tetranychus cinabarius**, **Meloidogyne incognita acrita**, and **Musca domestica** among tested insects were generally sensitive against these chemicals.

Among 2-morpholinones

phenyl group at C 6 had the insecticidal activity to some extent.

cinabarius
inones.

2-morphol-

Table 7 Insecticidal activity of some N-substituted aminoalcohols.

Insect No. Compds. No.	1			2				6		7		8
	1	1b		2	3	4	5	6		2000	500	
Concn. (ppm)	2000	500	2000	2000	2000	2000	2000	2000	2000	2000	500	
1	57.9	43.2	2.2	5	20	0	0	48	52	52.9	0	
2	22.0	23.4	2.2	20	20	0	0	58	50	61.5	7.1	
3	40.0	22.7	1.3	0	20	0	0	40	53	81.3	7.7	
4	86.4*	36.4	5.6	0	30	0	0	38	61	77.8	0	
5	70.7	20.0	2.1	5	30	0	0	50	55	80.0	6.7	
6	42.1	35.6	2.4	0	10	0	0	60	54	50.0	0	
7	43.2*	25.6	0	0	40	0	0	77	56	56.3	7.7	
8	45.3*#	16.1	36.3	10	0	0	0	50	46	68.8	12.5	
9	28.6	14.3	4.3	20	10	0	0	55	54	38.9	0	
10	78.4*	72.0	2.0	0	10	0	0	51	56	73.7	26.7	
Control	4.8		1.0	0	0	0	0	56	53	6.3		0
Time (day)	2	2	7	2		22	2	30	30	2	2	2

* plant injury, # herbicidally active to barnyard grass (100% inhibition at 100 ppm).

Table 8. Insecticidal activity of some 2-morpholinones.

Insect No. Compds.No.		lb	2	3	4	7
Concn. (ppm)	2000 500	2000 500	2000 2000 2000	2000 2000 2000	2000 500	
11		1.3 1.4	15.3 0 0	7.1 0		
12		12.3 1.2	13.4 10.0 0	0 0		
13		0 1.1	10.9 0.1 0	0 0		
14	9.4 9.7	4.1 0	12.5 0 0	0 0		
	6.6	1.2 0	13.9 0 0	7.1 0		
		1.3 1.3	11.5 0 0	5.9 0		
17		a.3 1.3	18.5 0 0	0 0		
18		18.4 0	13.1 0 0	5.6 0		
19		8.0 7.0	11.3 0 0	5.3 0		
20		4.9 0	11.0 0 0	5.3 0		
21		0 2.4	17.1 10.0 0	7.1 0		
22		0 3.5	11.3 0 0	11.8 0		
23		3.4 0	11.8 0 0	0 6.3		
24		1.0 0	13.3 10.0 0	10.0 7.1		
25		3.3 0	9.2 0 0	0 0		
26		0 0	14.1 0 0	0 7.1		
27		1.4 0	15.1 10.0 0	12.5 0		
29		0 0	13.7 0 0	0 0		
30		5.9 0	13.9 0 0	7.1 0		
31		4.1 0	10.9 9.1 0	6.3 15. a		
32		0 1.3	13.0 0 0	5.0 0		
33		4.2 0	10.4 0 0	13.3 0		
34	31.7 7.7	1.1 1.4	12.9 10.0 0	0 0		
35	25.0 10.0	0 0	10.7 0 0	0 0		
36	21.7 12.7	6.5 3.3	15.4 20.0 0	7.1 0		
37	11.3 6.9	0 0	11.8 0 0	0 0		
38	25.5 6.9	0 0	14.2 10.0 0	13.3 0		
39	12.3 1.4	3.9 1.3	10.2 0 0	0 5.3		
40	28.3 15.8	1.2 0	11.6 0 0	5.0 0		
HCON(Me) ₂	a.5 —	0 —	11.3 0 0	0 0		
	3.2 0	0 —	11.8 0 0	0 —		

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