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The Rotational and Configurational Isomerism of *N*-(Monosubstituted ethyl)-amides by Nuclear Magnetic Resonance

JOSÉ M. AGUIRRE,[a] ADRIANA F. IBAÑEZ, ELBA N. ALESSO, DORA G. TOMBARI and GRACIELA Y. MOLTRASIO IGLESIAS*,[b]

Universidad Nacional de Luján,[a] Luján, Argentina, and Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires,[b] Junín 956, Capital Federal, Argentina

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Several *N*-(monosubstituted ethyl)amides were synthesized and their carbon and proton nuclear magnetic resonance (^{13}C and ^{1}H-NMR) spectra were determined. Both (*Z*) and (*E*) stereoisomers could be observed in the formamides, but only the (*Z*) isomer was identified in the acetamides and phenylacetamides. The main body of the ^{1}H-NMR results indicated that the methylene protons were equivalent. This finding is interpreted in terms of free rotation around the $-CH_2-\dot{C}H-$bond and magnetic equivalence. In cases where the ^{1}H-NMR spectra revealed and ABX pattern, an interpretation is offered based on different populations among "pure staggered" conformers.

Keywords——*N*-(monosubstituted ethyl)amide; conformation; rotamer population; folded conformation; (*Z*)-(*E*) isomer; ^{13}C-NMR; ^{1}H-NMR

Several amides have been synthesized[1] during our studies on the competition between the Bischler–Napieralski and retro-Ritter reactions. This paper describes ^{1}H- and ^{13}C-nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) analyses of the amides of types I and II (Fig. 1) along with the conformational equilibria around the single bond $-CH_2-\dot{C}H-$ of the type I amide.

In the series of compounds RHN–CO–R′, when R′=H the ^{1}H-NMR results (Table I) showed a pair of (*Z*)-(*E*) diastereoisomers (Fig. 2). The more abundant form was invariably characterized by the lower ^{3}J(HH) value (1.7—2.1 Hz), while the less abundant form had the greater ^{3}J(HH) value (10—12 Hz).[2] The (*Z*) configuration must therefore be assigned to the more abundant isomer. When R′≠H, only the (*Z*) isomer was obtained, irrespective of R.

The results for the ^{13}C chemical shift[2] are summarized in Table II. It is interesting to note that the R′ change induced the same variation for ^{13}C=O whatever the *N*-alkyl substitution. Thus, replacing H by R′ induced a constant low-field shift in the series investigated. Moreover, in the (*Z*) isomer the carbonyl resonance was invariably at a lower frequency than that in the (*E*) configuration. As a rule, shielding of carbons α and β to the nitrogen atom was observed for the (*Z*) isomer. This shielding approached 5.0 ppm for C_α and 1.2 ppm for C_β of the type I amide and 4.4 ppm for C_α and 2.2 ppm for C_β of the type II amide.

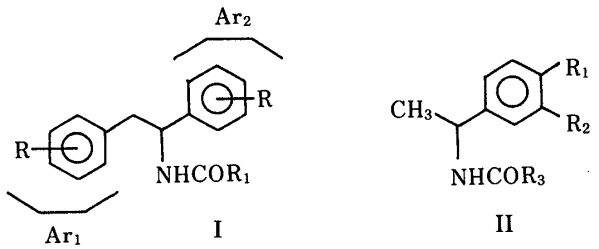

Fig. 1. The Two Types of Amides

Fig. 2. Configurational Isomerism of the Amides

TABLE I. Chemical Shifts of the Aliphatic Protons of the Types I and II Amides [δ (ppm)]

Amide	Ar_1	Ar_2	R_1	R_2	R_3	Isom.	H_α	H_β	NH	R_1	System
Type I											
1	Ph	Ph	H			(*Z*)	5.25	3.05	6.5	7.95	A_2MX
						(*E*)	4.55	3.00	6.5	7.75	A_2MX
2	Ph	Ph	CH_3			(*Z*)	5.25	3.05	6.4	1.85	A_2MX
3	Ph	Ph	Ph			(*Z*)	5.46	3.22	6.48	—	A_2MX
4	Ph	Ph	CH_2Cl			(*Z*)	5.25	3.15	7.00	4.00	A_2MX
5	Ph	Ph	CH_2Ph			(*Z*)	5.25	2.7—3.2	5.67	3.50	ABMX
6	Ph	Ver	H			(*Z*)	5.25	3.05	6.40	8.05	A_2MX
						(*E*)	4.61	3.02	6.40	7.90	A_2MX
7	Ph	Ver	CH_3			(*Z*)	5.20	3.08	5.80	1.95	A_2MX
8	Ph	Ver	CH_2Ph			(*Z*)	5.15	2.7—3.2	5.65	3.50	ABMX
9	An	Ver	H			(*Z*)	5.25	3.05	6.30	8.10	A_2MX
						(*E*)	4.62	3.01	6.30	7.90	A_2MX
10	An	Ver	CH_3			(*Z*)	5.15	3.00	5.73	1.90	A_2MX
11	An	Ver	CH_2Ph			(*Z*)	5.15	2.6—3.1	5.65	3.50	ABMX
12	Ver	Ph	H			(*Z*)	5.30	3.05	6.10	8.10	A_2MX
						(*E*)	4.70	3.01	6.10	7.90	A_2MX
13	Ver	Ver	H			(*Z*)	5.25	3.05	5.95	8.15	A_2MX
						(*E*)	4.60	3.00	5.95	7.87	A_2MX
14	Ver	Ver	CH_3			(*Z*)	5.10	3.00	6.15	1.90	A_2MX
15	Ver	Ver	CH_2Ph			(*Z*)	5.15	2.90	5.75	3.45	A_2MX
16	*p*-BrPh	Ver	H			(*Z*)	5.22	3.07	6.04	8.12	A_2MX
						(*E*)	4.60	3.02	6.04	7.89	A_2MX
17	*p*-BrPh	Ver	CH_3			(*Z*)	5.13	2.7—3.3	6.00	1.93	ABMX
18	*p*-BrPh	Ver	CH_2Ph			(*Z*)	5.10	2.80	5.55	3.40	A_2MX
19	*p*-NO_2Ph	Ver	H			(*Z*)	5.25	2.8—3.5	5.85	8.17	ABMX
						(*E*)	4.65	2.8—3.5	5.85	7.75	ABMX
20	*p*-NO_2Ph	Ver	CH_3			(*Z*)	5.20	3.0—3.5	6.05	2.00	ABMX
21	*p*-NO_2Ph	Ver	CH_2Ph			(*Z*)	5.20	3.05	5.64	3.50	A_2MX
22	Ver	*p*-NO_2Ph	H			(*Z*)	5.40	3.05	6.00	8.20	A_2MX
						(*E*)	4.60	3.00	6.00	8.20	A_2MX
Type II											
23			OCH_3	OCH_3	H	(*Z*)	5.10	1.45	6.20	8.05	m
						(*E*)	4.55	1.52	6.20	8.05	m
24			OCH_3	OCH_3	CH_3	(*Z*)	4.95	1.40	6.10	1.83	m
25			OCH_3	OCH_3	Ph	(*Z*)	5.30	1.60	6.45	—	m
26			CH_3	H	H	(*Z*)	5.20	1.45	6.25	8.05	m
						(*E*)	4.50	1.50	6.25	8.00	m

Ver, 3,4-dimethoxyphenyl. An, 4-methoxyphenyl.

At room temperature and in deuterochloroform solution, two general types of ^{1}H-NMR spectra were obtained for these amides: and ABX with eleven lines and an A_2X with five lines, disregarding NH–CH coupling ($J_{NH-CH} \simeq 7.8$ Hz).[1] The ABX spectra were analyzed in a prescribed manner.[3] For these spectra, values of both J_{ax} and J_{bx}, as well as J_{ab} (Fig. 3), are given in Table III. The highest field proton was taken as the b proton. The calculated parameters for some spectra (amides **16** and **17**) were fed into a computer program which yielded a close agreement between the calculated and observed spectra. Various sign combinations for J_{ax} and J_{bx} are also subjected to computer analysis, when only the computed intensities for J_{ax} and J_{bx} with like signs agreed with the observed spectra, with the exception of the amide **5**. Such ABX spectra suggest either that the molecules rotate about the C–C bond sufficiently quickly to make the hydrogen resonances coalesce or that the molecules are

TABLE II. Chemical Shifts of the Aliphatic Carbons of the Types I and II Amides [δ (ppm)]

Amide	Isomer (*Z*)			Isomer (*E*)		
	C_α	C_β	C=O	C_α	C_β	C=O
1	53.09	42.28	160.45	58.10	43.57	164.23
2	54.40	42.40	169.20			
3	54.70	42.50	166.60			
5	53.90	42.50	169.90			
6	53.12	42.67	160.78	58.18	43.94	164.18
7	54.07	42.33	169.06			
12	53.37	42.10	160.77	58.31	43.35	164.53
17	53.62	41.70	168.33			
23	46.56	21.27	160.02	50.99	23.48	163.81
24	47.86	21.30	168.86			
25	48.62	21.28	166.36			
26	46.35	21.13	160.40	50.74	22.52	163.69

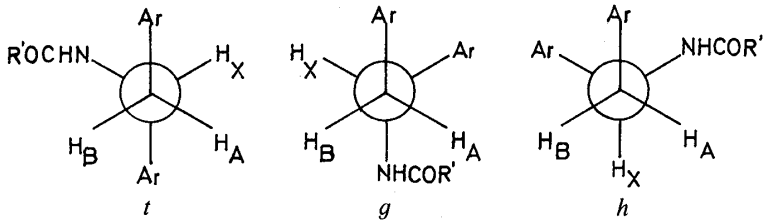

Fig. 3. Three Staggered Rotamers of the Amides

all in one of the possible conformations. That the first explanation is the correct one, in this family of amides, was demonstrated by observing the resonance spectra at low temperature. At -30 °C the spectral lines began to broaden, and at -50 °C they became split into several lines. The frequencies of the A_2X spectra were calculated by the standard method.[4]

The three most probable rotamers of *N*-acyl-1,2-diarylethylamines are shown in Fig. 3. The symbols *t*, *g* and *h* designate the mole fractions of a *trans* (*t*) and two *gauche* (*g* and *h*) rotamers, respectively.

Examination of Dreiding models of these rotamers suggested that there is no substantial hindrance to rotation around the ethane linkage. Assuming rapid interconversion of the three rotamers, the experimental coupling constants can therefore be represented as:

$$J_{ax}=tJ_g+gJ_t+hJ_g \tag{1}$$

$$J_{bx}=tJ_t+gJ_g+hJ_g \tag{2}$$

By considering two limiting cases in the rotamer distribution,[5] (I) $t=g=h$ and (II) $t=g\gg h$, Eqs. 1 and 2 can be simplified: substitution of these limitations into Eqs. 1 and 2 yields, for the designated cases,

(I) $J_{ax}=J_{bx}$

(II) $J_{ax}=tJ_g+gJ_t$

$J_{bx}=tJ_t+gJ_g$

The ratio $r=J_{ax}/J_{bx}$ is given by:

$$r=\frac{tJ_g+gJ_t}{tJ_t+gJ_g}$$

If it is assumed[6] that $J_t \simeq J_0 \cos^2 \varphi t$ and $J_g \simeq J_0 \cos^2 \varphi g$, it follows that the constant equilibrium between the two forms t and g is given by:

$$K = \frac{g}{t} = \frac{1-0.18r}{r-0.18}$$

Table III lists the values calculated for t and g from the experimental parameters. Calculated values for J_t and J_g are also given in Table III, and the average values for these J_t and J_g are in close agreement with those generally used for similar systems.[7]

Inspection of Table I shows that the formamides and acetamides almost exclusively exhibit an A_2X pattern. As a rule, magnetic nonequivalence due to molecular asymmetry of A and B protons implies that $\Delta \nu ab = \nu b - \nu a = 0$, even when the rotamer populations are equal. For the cases presented in this paper, it may be concluded from the results of spin–spin coupling analysis that the rotamer populations are equal, so that the rotameric conformations differ only slightly in energy. Since $\Delta \nu = 0$, the magnetic nonequivalence is evidently very small (less than the limit that our instruments can discern). In the cases of the amides **17**, **19**, and **20**, it can be argued that a dipole interaction between the carbonyl and the *p*-nitrophenyl or *p*-bromophenyl groups is the major factor responsible for the ABX-type spectra.

Quite a different situation is observed for the phenylacetamides (**5**, **8** and **11**). Data currently available rule out an unambiguous interpretation of the mechanism by which the benzyl group changes the spectral pattern (from A_2X to ABX and *vice versa*). One possible explanation for this conformational preference in the amides **5**, **8** and **11** is the folded conformation illustrated in Fig. 4, forced by the benzyl group.[8] There is thus a direct interaction between the aromatic ring bonded to C_β and the amide bond. Proton magnetic resonance studies of amides in aromatic solvents have consistently demonstrated that there is an attraction between solute and solvent[9] as a result of a dipole-induced dipole interaction. This finding, though unconfirmed, is supported by the measurement of the ^{1}H-NMR of the amides **5**, **8** and **11** in dimethylsulfoxide-d_6 (DMSO-d_6), which indicated that the protons became equivalent. On the basis of the dipole-induced dipole mechanism, DMSO ($\mu = 3.9$) should compete with the amide for the aromatic ring and thus tend to destabilize the folded

Table III. Proton Magnetic Resonance-Calculated Parameters and Populations

Amide	H_a [δ (ppm)]	H_b [δ (ppm)]	$\Delta\nu$	J_{ax}	J_{bx}	J_{ab}	J_g	J_t	g	t
					(Hz)				(%)	
5	3.00	2.84	12.36	−6.59	8.97	12.73	2.35	13.20	39	61
8	2.92	2.83	9.71	5.55	7.46	14.01	2.30	10.60	38	62
11	2.98	2.90	8.25	5.77	6.75	14.01	1.91	10.61	44	56
17	3.07	2.97	8.00	5.69	8.89	13.59	2.16	12.35	34	66
19	3.32	3.17	11.92	6.13	8.09	13.55	2.21	12.03	40	60
20	3.30	3.13	13.41	6.90	9.16	13.25	2.30	10.60	39	61

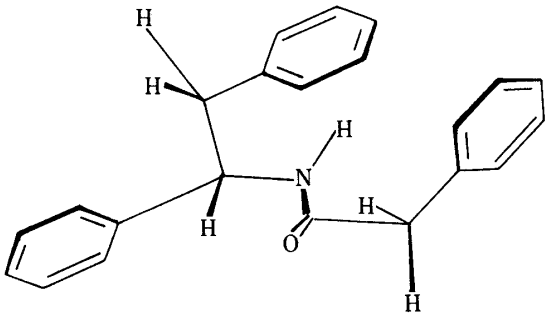

Fig. 4. Folded Conformation for Phenylacetamides

form. Finally it should be borne in mind that such attraction between the amides and aromatic solvents is absent when the solvent is *p*-nitrobenzene, and is very slight for veratrol.[10]

Experimental

Infrared spectra were obtained with a Shimadzu IR 440 spectrometer. In all cases, the samples were examined as a mull (Nujol) and the results are reported in cm^{-1}. The ^1H- and ^{13}C-NMR spectra were recorded with a Bruker WO 80 SYFT or a Varian FT 80 A spectrometer employing Cl_3CD as the solvent. The spectra were referenced to internal Me_4Si and are reported on the δ scale. Some of our derived parameters were checked on the computer program, Spin Simulation (SIMEQ) FT-80 A.

Elemental analyses were carried out in our laboratories using a Coleman analyzer. Melting points (uncorrected) were obtained with a Thomas Hoover apparatus.

1-(3,4-Dimethoxyphenyl)-2-(4-nitrophenyl)ethanone——This was synthesized from 4-nitrophenylacetic acid and veratrol with polyphosphoric acid.[1] Yield 76%, mp 153—154 °C (benzene–hexane). IR: 1680 (C=O), 1530 and 1360 (N–O). ^1H-NMR: 3.90 (3H, s, OCH_3), 3.95 (3H, s, OCH_3), 4.35 (2H, s, CH_2), 6.85 (1H, d, J=8.5 Hz, Ar), 7.37 (2H, d, J=9.5 Hz, Ar), 7.47 (1H, s, Ar), 7.6 (1H, d, J=8.5 Hz, Ar), 8.13 (2H, d, J=9.5 Hz, Ar). *Anal.* Calcd for $C_{16}H_{15}NO_5$: C, 63.77; H, 5.02; N, 4.65. Found: C, 63.52; H, 5.05; N, 4.70.

1-(4-Nitrophenyl)-2-(3,4-dimethoxyphenyl)ethanone——Synthesis was performed according to the method of Zimmer and Bercz.[11] Yield 60%, mp 123—124 °C (EtOH). IR: 1690 (C=O), 1510 and 1340 (N–O). ^1H-NMR: 3.85 (6H, s, OCH_3), 4.25 (2H, s, CH_2), 6.75 (3H, m, Ar), 8.20 (4H, m, Ar). *Anal.* Calcd for $C_{16}H_{15}NO_5$: C, 63.77; H, 5.02; N, 4.65. Found: C, 63.79; H, 5.03; N, 4.62.

***N*-[1-(3,4-Dimethoxyphenyl)-2-(4-nitrophenyl)ethyl]formamide (19)**——This was prepared from the respective ketone in the usual manner.[1] Yield 80%, mp ((*Z*) isomer) 170—172 °C (EtOH). IR: 3280 (NH), 1650 (C=O), 1510 and 1350 (N–O). ^1H-NMR: ((*Z*) isomer); 3.17 (1Hb, dd, CH_2), 3.32 (1Ha, dd, CH_2), 3.85 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 5.25 (1H, br q, CH), 5.85 (1H, br d, NH), 6.70 (3H, m, Ar), 7.25 (2H, d, J=8.5 Hz, Ar), 8.08 (2H, d, J=8.5 Hz, Ar), 8.17 (1H, s, CHO). *Anal.* Calcd for $C_{17}H_{18}N_2O_5$: C, 61.81; H, 5.94; N, 8.48. Found: C, 61.73; H, 5.87; N, 8.45.

***N*-[1-(4-Nitrophenyl)-2-(3,4-dimethoxyphenyl)ethyl]formamide (22)**——This was prepared from the respective ketone in the usual manner.[1] Yield 56%, mp ((*Z*) isomer) 141—142 °C (MeOH). IR: 3320 (NH), 1660 (C=O), 1530 and 1340 (N–O). ^1H-NMR: ((*Z*) isomer); 3.05 (2H, d, J=7.8 Hz, CH_2), 3.75 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 5.40 (1H, br q, CH_2), 6.00 (1H, br d, NH), 6.65 (3H, m, Ar), 7.37 (2H, d, J=8.5 Hz, Ar), 8.17 (2H, d, J=8.5 Hz, Ar), 8.20 (1H, s, CHO). *Anal.* Calcd for $C_{17}H_{18}N_2O_5$: C, 61.81; H, 5.94; N, 8.48. Found: C, 61.72; H, 5.96; N, 8.51.

***N*-[1-(3,4-Dimethoxyphenyl)-2-(4-nitrophenyl)ethyl]acetamide (20)**——A mixture of 3.1 g (9 mmol) of formamide **19**, HCl (37 ml, *d* 1.19) and water (117 ml) was heated at reflux for 6 h. The clear solution on cooling afforded the product as the chlorhydrate. After filtration the sample was dried. The acetylated derivative was prepared in the usual manner.[1] Yield 65%, mp 145—146 °C (EtOH). IR: 3325 (NH), 1665 (C=O), 1530 and 1350 (N–O). ^1H-NMR: 2.00 (3H, s, CH_3), 3.13 ($1H_b$, dd, CH_2), 3.30 ($1H_a$, dd, CH_2), 3.80 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 5.20 (1H, br q, CH), 6.05 (1H, br d, NH), 6.75 (3H, m, Ar), 7.20 (2H, d, J=8.5 Hz, Ar), 8.05 (2H, d, J=8.5 Hz, Ar). *Anal.* Calcd for $C_{18}H_{20}N_2O_5$: C, 62.78; H, 5.85; N, 8.13. Found: C, 62.70; H, 5.81; N, 8.09.

General Procedure for the Synthesis of Phenylacetamides——The corresponding formamide (1 mmol) was treated with HCl (10%) and then heated at reflux to give a solution. On cooling, the precipitate was dried and treated with a solution of phenylacetyl chloride (1 mmol) in benzene–pyridine (10 : 0.1) in the usual manner.

***N*-[1-(3,4-Dimethoxyphenyl)-2-phenylethyl]phenylacetamide (8)**——Yield 80%, mp 160—161 °C (EtOH). IR: 3320 (NH), 1660 (C=O). ^1H-NMR: 2.83 ($1H_b$, dd, CH_2), 2.92 ($1H_a$, dd, CH_2), 3.50 (2H, s, CH_2–Ph), 3.70 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 5.15 (1H, br q, CH), 5.65 (1H, br d, NH), 6.4—7.5 (13, m, Ar). *Anal.* Calcd for $C_{24}H_{25}NO_3$: C, 76.77; H, 6.71; N, 3.74. Found: C, 76.83; H, 6.74; N, 3.70.

***N*-[1-(3,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)ethyl]phenylacetamide (11)**——Yield 75%, mp 159—160 °C (EtOH). IR: 3325 (NH), 1650 (C=O). ^1H-NMR: 2.90 ($1H_b$, dd, CH_2), 2.98 ($1H_a$, dd, CH_2), 3.50 (2H, s, CH_2Ph), 3.70 (3H, s, OCH_3), 3.74 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 5.15 (1H, br q, CH), 5.65 (1H, br d, NH), 6.40—6.80 (7H, m, Ar), 7.06—7.38 (5H, m, Ar). *Anal.* Calcd for $C_{25}H_{27}NO_4$: C, 74.05; H, 6.71; N, 3.46. Found: C, 74.15; H, 6.79; N, 3.50.

***N*-[1,2-Bis(3,4-dimethoxyphenyl)ethyl]phenylacetamide (15)**——Yield 70%, mp 170—171 °C. IR: 3320 (NH), 1645 (C=O). ^1H-NMR: 2.90 (2H, d, CH_2), 3.45 (2H, s, CH_2Ph), 3.65 (3H, s, OCH_3), 3.70 (3H, s, OCH_3), 3.80 (6H, s, OCH_3), 5.15 (1H, br q, CH), 5.75 (1H, br d, NH), 6.20—6.75 (7H, m, Ar), 6.90—7.25 (4H, m, Ar). *Anal.* Calcd for $C_{26}H_{29}NO_5$: C, 71.70; H, 6.71; N, 3.22. Found: C, 71.68; H, 6.74; N, 3.12.

***N*-[1-(3,4-Dimethoxyphenyl)-2-(4-bromophenyl)ethyl]phenylacetamide (18)**——Yield 80%, mp 196—197 °C (EtOH). IR: 3325 (NH), 1650 (C=O). ^1H-NMR: 2.80 (2H, d, J=7.7 Hz, CH_2), 3.40 (2H, s, CH_2Ph), 3.65 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 5.10 (1H, br q, CH), 5.55 (1H, br d, NH), 6.40 (1H, s, Ar), 6.50—6.75 (4H, m, Ar), 7.00—

7.30 (7H, m, Ar). *Anal.* Calcd for $C_{24}H_{24}BrNO_3$: C, 63.44; H, 5.33; N, 3.09. Found: C, 63.34; H, 5.31; N, 3.05.

***N*-[1-(3,4-Dimethoxyphenyl)-2-(4-nitrophenyl)ethyl]phenylacetamide (21)**——Yield 70%, mp 181—182 °C (EtOH). IR 3320 (NH), 1660 (C=O), 1530 and 1355 (N–O). ^{1}H-NMR: 3.05 (2H, d, J=7.8 Hz, CH_2), 3.50 (2H, s, CH_2Ph), 3.76 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 5.20 (1H, br q, CH), 5.64 (1H, br d, NH), 6.46—6.80 (3H, m, Ar), 6.94—7.38 (7H, m, Ar), 7.96 (2H, d, J=8.5 Hz, Ar). *Anal.* Calcd for $C_{24}H_{24}N_2O_5$: C, 68.55; H, 5.76; N, 6.66. Found: C, 68.51; H, 5.78; N, 6.59.

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References

1) J. M. Aguirre, E. N. Alesso, D. G. Tombari, A. F. Ibañez, J. D. Bonafede and G. Y. Moltrasio Iglesias, *An. Asoc. Ouím. Argent.*, **75**, 393 (1987).
2) J. Done, J. P. Gouesnard, B. Mechun, N. Naulet and G. Y. Martin, *Org. Mag. Res.*, **13**, 126 (1980).
3) H. Gunther, "NMR Spectroscopy," John Wiley and Sons, Inc., New York, 1979.
4) L. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed., Pergamon Press, Inc., New York.
5) R. B. Martin and R. Mathur, *J. Am. Chem. Soc.*, **87**, 1065 (1965).
6) B. Clin, B. Jousseaume and J. G. Duboudin, *Bull. Soc. Chim. Fr.*, **1974**, 1293.
7) T. Sasaki, K. Kanematsu, Y. Tsuzuki and K. Tanaka, *J. Med. Chem.*, **9**, 847 (1966).
8) K. D. Kopple and D. H. Marr, *J. Am. Chem. Soc.*, **89**, 6193 (1967).
9) J. V. Hatton and W. G. Schneider, *Can. J. Chem.*, **40**, 3285 (1962).
10) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **5**, 139 (1962).
11) H. Zimmer and J. P. Bercz, *Justus Liebigs Ann. Chem.*, **686**, 107 (1965).