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NMR spectra of substituted ureas

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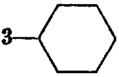
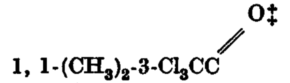
Abstract—The NMR spectra of a number of dimethylureas are reported.

As a result of studies on the structure of pactamycin, there was an indication that 1, 1-dimethylureas have NMR spectra in which the two methyl groups appear as a singlet in contrast to analogous amides. A search of the literature revealed that the NMR spectrum of only one urea of this type had been reported [1]. The single example was tetramethylurea, which gave a singlet but, being completely symmetrical, could be an atypical example. It has long been known [2] that the NMR spectra doublets of N, N-dimethylamides are due to restricted rotation around the central C—N bond, so it was assumed that the NMR spectra of ureas could be used to study the degree of restricted rotation present. Investigations on ureas [3] have been too limited to establish whether or not such restriction exists with this class of compounds. Brown and Katekar [4] have shown that thioureas do show restricted rotation about a central C—N bond at lower temperatures with acyl ureas showing greater resistance to rotation than do alkyl or aryl analogs. Accordingly, the NMR spectra of a number of representative ureas were run at two temperatures, primarily to establish the nature of the peak due to the two methyl groups and, secondarily, to get some indication of the extent of any restricted rotation occurring.

Eleven ureas (Table 1) were studied, of which one was an acyl urea and all but one were 1,

Table 1

Urea	Chemical shifts* Operating temp.	−40°C
$1, 1\text{-}(CH_3)_2\text{-}3\text{-}CH_3$	2.90	2.95†
$1, 1\text{-}(CH_3)_2\text{-}3\text{-}C_2H_5$	2.86	2.93
$1, 1\text{-}(CH_3)_2\text{-}3$ 	2.90	2.93
 $1, 1\text{-}(CH_3)_2\text{-}3\text{-}Cl_3C\overset{O‡}{C}$	2.98	3.02
$1, 1\text{-}(CH_3)_2\text{-}3\text{-}\phi$	2.97	3.07
$1, 1\text{-}(CH_3)_2\text{-}3\text{-}p\text{-}CH_3O\phi$	2.92	2.92
$1, 1\text{-}(CH_3)_2\text{-}3\text{-}p\text{-}NO_2\phi^c$	2.98	3.11
$1, 1\text{-}(CH_3)_2\text{-}3, 3\text{-}(CH_3)_2$	2.85	2.85
$1, 1\text{-}(CH_3)_2\text{-}3, 3\text{-}(C_2H_5)_2$	2.85	2.80
$1, 1\text{-}(CH_3)_2\text{-}3, 3\text{-}(CH_2)_5$	2.88	2.83
$1, 3\text{-}(CH_3)_2\text{-}1, 3\text{-}(C_2H_5)_2$	2.77	2.82

* Chemical shift values are for the methyl groups except for the 3-methyl in the first compound and are expressed in delta units, ppm relative to internal TMS. The instrument used was a Varian A-60.

† Run at −50°.

‡ Run in d_7DMF. All others were run in $CDCl_3$.

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[1] M. J. D. Low and L. Abrams, *Appl. Spectry* **20**, 414 (1966).

[2] W. D. Phillips, *J. Chem. Phys.* **23**, 1363 (1955).

[3] (a) C. R. Redpath and J. G. S. Smith, *Trans. Faraday Soc.* **58**, 462 (1962); (b) T. Birchall and R. J. Gillespie, *Can. J. Chem.* **41**, 2642 (1963).

[4] B. L. Brown and G. F. Katekar, *Tetrahedron Lett.* 2343 (1969).

1-dimethylureas. Nine of the ureas were known (although in three cases, characterization data were absent or meager) and were obtained commercially or synthesized by standard procedures. The new trisubstituted urea was prepared by the reaction of dimethylamine with trichloroacetyl isocyanate. The new tetrasubstituted urea was obtained from the reaction of dimethylcarbamoyl chloride with piperidine. The melting or boiling points of the new ureas and their analyses are shown in Table 2 as well as data from ureas which have been reported in the literature, but have not been well characterized.

Table 2

Urea	Yield (%)	M.p. or B.p. (°C)	Calc. (%)			Calc.	Found (%)			Found
			C	H	N	Mol. wt	C	H	N	Mol. wt.
1, 1-$(CH_3)_2$-3-Cl_3CCO	27	152	25.77	3.03	45.65*	233.5	25.95	3.03	45.74*	232
1, 1-$(CH_3)_2$-3-p-$NO_2\phi$†	92	220	51.67	5.30	20.09	209.0800	51.73	5.39	19.72	209.0794
1, 1-$(CH_3)_2$-3-C_2H_5‡	25	48–53	51.70	10.41	24.12	116.0950	51.37	10.34	23.78	116.0952
1, 1-$(CH_3)_2$-3, 3-$(CH_2)_5$	88	111/17 mm	61.50	10.32	17.93	156.1262	61.18	11.00	17.21	156.1262
1, 3-$(CH_3)_2$-1, 3-$(C_2H_5)_2$‡	45	83/17 mm	58.30	11.18	19.43	144.1262	58.22	10.96	18.71	144.1264

* Chlorine instead of N.

† This compound has been mentioned several times in the literature, but its preparation and characterization have not been reported.

‡ These compounds have been reported, but the only physical property given was incorrect.

Seven trisubstituted 1, 1-dimethylureas were studied, being divided among 3-alkyl-, 3-aryl-, and 3-acyl-types. Four tetrasubstituted ureas were observed, of which three were 1, 1-dimethyl-3, 3-dialkylureas and the other was 1, 3-dimethyl-1, 3-diethylurea. Spectra were run at the normal operating temperature of the instrument and at −40°C. The solvent was usually $CDCl_3$, but in two cases d_7DMF was used. In all cases at both temperatures, only a singlet was observed for the two methyl groups (Table 1). These results indicate that in 1, 1-dimethylureas over a considerable range of temperatures, there is free rotation about the C—N bond directed toward the methyl groups. It is possible that there is restricted rotation about the other central C—N bond, but there was no indication of it in these studies. Interestingly, the 1, 1-dimethyl-3, 3-diethylurea spectra and the 1, 3-dimethyl-1, 3-diethylurea spectra were surprisingly similar.

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Optical absorption spectrum of iron in beryl

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Abstract—The optical absorption spectrum of Fe^{3+} in beryl has been studied at room and liquid air temperatures. The cubic field approximation with $Dq = 1320\ cm^{-1}$, $B = 720\ cm^{-1}$ and $C = 4{\cdot}45B$ is found to give a good fit to the observed band positions.

INTRODUCTION

THE paramagnetic resonance and optical spectrum of iron in beryl has been investigated by DVIR and LOW [1]. Beryl grows in hexagonal crystals. Its structure has been studied in detail

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[1] M. DVIR and W. LOW, *Phys. Rev.* **119**, 1587 (1960).