Tetrahedron Letters No. 20, pp. 1651-1652, 1971. Pergamon Press. Printed in Great Britain.

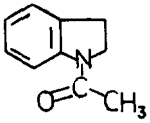
CONFORMATION OF 1,3-DIACYL AND 1,3-DIAROYLBENZIMIDAZOLONES

Makhluf J. Haddadin and Adil A. Jarrar

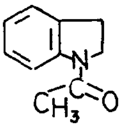
Department of Chemistry, American University of Beirut, Beirut, Lebanon

(Received in UK 30 March 1971; accepted for publication 6 April 1971)

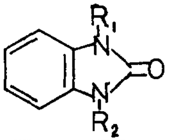
Assignment of conformations of rotamers in amides has recently been reported by Monro and Sewell[1] using NMR, and confirmed by Jones, Katritzky, and Shapiro[2] through dipole measurements. Both teams concluded that, at ambient temperature, 1-acetylindoline exists almost entirely in the endo conformation I, whereas 1-acetyl-1,2,3,4-tetrahydroquinoline consists of about equal quantities of the endo III and the exo IV conformers. Monro and Sewell inferred that the area under the H_7 signal (deshielded by 1.73-1.57 τ compared with the H_7 in indoline) represented the fraction of molecules in the endo conformation I.

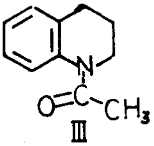


I

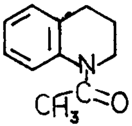


II





III



IV

No.	R_1	R_2	Chemical shift (τ) for H_4 or/and H_7	$\triangle$
V	H	H	3.0	0
VI	CH_3CO	PhCO	1.7	-1.3
VII	C_2H_5CO	"	1.65	-1.35
VIII	$(CH_3)_2CHCO$	"	1.75	-1.25
IX	t-BuCO	"	2.0 Estimated	-1.0
X	PhCO	PhCO	2.1 "	-0.9
XI	CH_3CO	CH_3CO	1.75	-1.25
XII	$(CH_3)_2CHCO$	$(CH_3)_2CHCO$	1.7	-1.3
XIII	t-BuCO	t-BuCO	2.28	-0.72
XIV	o-$CH_3C_6H_4CO$	o-$CH_3C_6H_4CO$	1.8	-1.2
XV	o-$NO_2C_6H_4CO$	o-$NO_2C_6H_4CO$	1.55	-1.45
XVI	o-$MeOC_6H_4CO$	o-$MeOC_6H_4CO$	1.74	-1.26

During the photolysis of some substituted quinoxaline-di-N-oxides, we isolated the title compounds VI through X (see table) as products.[3] In each of the NMR spectra of products VI, VII, and VIII one aromatic proton was deshielded by about 1.3 τ units from the rest of the protons of the benzimidazolone nucleus. This deshielding effect dropped to about 1 unit in compounds IX and X. Examination of the molecular model of IX showed that overlap of the nitrogen lone pair with the acyclic carbonyl system causes the bulky t-butyl group to interact sterically either with H_7 (exo form) or with oxygen at C_3 (endo form). Tnerefore, it appears that the decrease in the deshielding effect here is due to a decrease in the double bond character of the amide linkage such as would permit the pivalyl group to rotate out of the plane of the heterocyclic ring system. Similar considerations apply for diamide X, where the phenyl ring competes with the nitrogen lone pair for conjugation with the carbonyl group, thus again reducing the double bond character of the amide linkage and decreasing the extent of deshielding. This interpretation is supported by the observation that ortho substituents on the benzoyl group (XIV, XV, and XVI) restore the original value ($\sim 1.3\ \tau$ units) for the deshielding of H_4 and H_7, as would be expected with a decrease of resonance interaction in the aroyl group and, therefore, an increase in the double bond character of the amide linkage.[4]

Furthermore, with symmetrically substituted compounds (XI and XII), we found appreciable deshielding at H_4 and H_7 ($\sim 1.3\ \tau$ units) as compared with the expected lower value observed for XIII ($0.72\ \tau$). It appears that the aliphatic amido moieties exist almost entirely in the endo conformation, in VI, VII, and VIII as well as in the (diendo) products XI and XII.

Although it is not clear why the acyl group in 1-acetylindoline favors the endo conformation, it seems logical that, in the absence of cross conjugation or unfavorable steric effects, the carbonyl groups in N-acyl or N,N-diacylbenzimidazolones exist in the endo conformation to minimize dipole-dipole interaction with the carbonyl group at C_3.[5]

Acknowledgment. The authors are grateful to Chas. Pfizer and Co. Inc. for a generous grant in support of this work, and thank Professor C.H. Issidorides for stimulating discussion.

References

1. A.M. Monro and M.J. Sewell, Tetrahedron Letters, 7, 595 (1969) and references cited therein.
2. R.A.Y. Jones, A.R. Katritzky, and B.B. Shapiro, Tetrahedron, 26, 721 (1970). See also H. Kessler, Angew. Chem. Intern. Edit., 9, 219 (1970), and W.E. Stewart and T.H. Siddal, III, Chem. Rev., 70, 517 (1970).
3. The results of this work will be reported later.
4. A.H. Lewin and M. Frucht, Tetrahedron Letters, 13, 1079 (1970).
5. Diacetyl derivatives of 1,2,3,4-tetrahydroquinoxaline seem to favor exo-conformations. The details of this study will be communicated in the near future.