involving reaction 4a or a single-step one utilizing 4d can readily be decided by comparing the *n*-hexylamine and the cyclohexylamine reactions. Reaction 4d is expected to more readily occur during the irradiation of cyclohexylamine than with *n*-hexylamine whether one considers the relative bond dissociation energies of the α-CH bonds or the stability of the resulting imine double bonds. Yet imine formation does not occur with cyclohexylamine. Consequently, it appears the reaction of *n*-hexylamine is using reaction 4a.

It is now possible to conclude that N–H bond rupture is the dominant primary reaction of the excited state *n*-hexylamine whereas C–N bond rupture is most important for the excited state of cyclohexylamine. Though less clear, it appears that cyclopentylamine occupies an intermediate reactivity position as expected.

We have no evidence from this work to support the esr observation of Richerzhagen and Volman[7] on the presence of the imine radical >C=N· during the photolysis of primary alkylamines in an adamantane matrix. Since they have presented evidence that this species is generated from the excitation of another radical, we assume the precursor radical is not allowed to build up under the conditions of these experiments as it is in either a matrix or in cold solution.

All the amines of this study have absorption only at the far end of the near-uv range of the spectrum. The absorbance of the pure amines commonly reach 2 at about 240 nm with considerable tailing to about 300 nm when the spectra are obtained in a 1-cm cell. Therefore it is desirable to use quartz irradiation vessels with the full output of the mercury arc to effect these reactions.

Registry No.—Cyclohexylamine, 108-91-8; cyclopentylamine, 1003-03-8; *n*-hexylamine, 111-26-2.

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Proton Magnetic Resonance Spectra of Aromatic *N,N*-Dimethylcarboxamides. Evidence for Hindered Rotation and Anisotropic Effects Caused by Additional Phenyl Rings[1]

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A previous publication from this laboratory[2] reported a large chemical shift difference (42 cps as compared to 10 cps for *N,N*-dimethylformamide) observed for the protons of the amide methyls in *N,N*-dimethyl-9-carboxamido-9,10-dimethylacridane. This seemingly abnormal chemical shift difference was explained on the basis of the preferred conformation of the amide function which places one of the methyls over the aromatic rings in the molecule. It was postulated that, owing to the diamagnetic anisotropic effect of the rings, the trans methyl experiences a long-range shielding effect, the methyl group cis to the carbonyl being unaffected. This then causes the net chemical shift difference to be large. As no report of the magnitude of such a shielding effect caused by additional phenyl rings has yet appeared, here we present a systematic study of the pmr spectra of aromatic *N,N*-dimethylcarboxamides containing up to three fused phenyl rings.

The results are summarized in Table I. The free energy of activation for rotation around the C–N bond ($\Delta G^{\ddagger}$) was calculated by the intensity ratio method.[3] It has been shown[4] that the $\Delta G^{\ddagger}$ values obtained by this method are quite reliable when the coalescence temperatures (T_c) are not too high. Unfortunately, the coalescence temperatures and hence $\Delta G^{\ddagger}$ for the anthracene (**5**) and acridine (**6**) amides could not be obtained, since these were much higher than the upper temperature limit for the solvent employed ($CDCl_3$). Use of a high-boiling solvent such as CBr_4 caused extensive decomposition before the coalescence temperatures were reached.

The pmr spectra of substituted *N,N*-dimethylbenzamides have been studied by Jackman, *et al.*[5] It has been shown that electron-donating substituents decrease $\Delta G^{\ddagger}$ while electron-withdrawing substituents increase it. As a nitrogen atom in an aromatic nucleus is known to be a strong electron withdrawer from the para position, it is expected to cause an increase in $\Delta G^{\ddagger}$. The data in Table I indicate that this expectation has been borne out. The ring-to-carbonyl group conjugation present in *N,N*-dimethylbenzamide is known to be responsible for its low C–N rotational barrier[5] (for example, $\Delta G^{\ddagger}$ for the benzamide[5] is 15.5 kcal mol^{-1} while for the formamide[3] it is 21 kcal mol^{-1}). The observed increase in T_c and $\Delta G^{\ddagger}$ with the increase in the number of phenyl rings (Table I) shows that the additional rings cause a decrease in this conjugation. The most likely explanation of this phenomenon probably lies in the steric interactions between the peri hydrogens of the additional rings and the methyl groups of the amide function. The resulting change in the conformation about the ring-to-carbonyl group bond causes an increase in the dihedral angle and hence reduction in the conjugation. This explanation is supported by the large $\Delta G^{\ddagger}$ (22.5 kcal mol^{-1}) observed for 2,4,6-trimethyl-*N,N*-dimethylbenzamide.[6] Steric factors are clearly seen to be predominant in this case.

In monosubstituted *N,N*-dimethylbenzamides, the values for $\Delta\delta$ increase with $\Delta G^{\ddagger}$ in a somewhat linear manner.[5] This is probably due to the increased rigidity with which the amide methyls are held over the phenyl ring. However, in the case of the amides in the present study, the increase in $\Delta\delta$ is too large to be accounted for by this effect alone. For example, $\Delta G^{\ddagger}$ for *p*-nitro-*N,N*-dimethylbenzamide[5] is 16.4 kcal mol^{-1}, compa-

(1) Presented in part at the 23rd Southeastern Regional Meeting of the American Chemical Society, Nashville, Tenn., Nov 4–5, 1971.

(2) G. A. Digenis and E. O. Magarian, *J. Pharm. Sci.*, **58**, 1026 (1969).

(3) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

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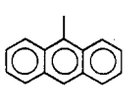
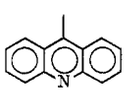
(5) L. M. Jackman, T. E. Kavanagh, and R. C. Haddon, *ibid.*, **1**, 109 (1969).

(6) A. Mannschreck, *Chem. Abstr.*, **63**, 6822*d* (1965).

TABLE I

PMR DATA FOR AMIDES $RC(=O)-NCH\delta_2$ ($CH_3\delta_1$) (0.5 *M* SOLUTIONS IN $CDCl_3$)

No.	R	Mp, °C	Chemical shifts of the methyl protons[a] δ_1	δ_2	$\frac{\delta_1+\delta_2}{2}$	$\Delta\delta$ ($\delta_2-\delta_1$)	T_c, °C	$\Delta G^{\ddagger}$, 298.2 kcal/mol	Shifts[d] induced by —Eu(DPM)$_3$, cps— Downfield CH_3	Upfield CH_3
1[b]		42	2.955	3.085	3.02	0.13	30	15.5	138	88
2		55	2.89	3.01	2.95	0.12	46	16.0	90	62
3		59	2.67	3.15	2.91	0.48	66	16.6	127	80
4		37	2.67	3.15	2.91	0.48	86	17.2	108	73
5		139	2.55	3.26	2.91	0.71	>95	*c*	99	65
6		172	2.69	3.40	3.05	0.71	>95	*c*	98	63

[a] From TMS as internal standard. [b] Data from ref 4 and 5. [c] Not available; see text. [d] $Eu(DPM)_3$/amide ratio = 0.3; 0.3 *M* amide in CCl_4.

rable to that for the naphthalene amide in the present study (16.6 kcal mol^{-1}). Yet the former amide exhibits $\Delta\delta$ of 0.16 ppm, far lower than that for the latter amide, 0.42 ppm. This increase in the values of $\Delta\delta$ with an increase in the number of phenyl rings probably reflects the anisotropic effect exerted by the additional rings, resulting in considerable long-range shielding of one of the methyls. A progressive decrease in δ_1 (Table I) is clearly seen. A more curious observation is the increase in δ_2, indicating a stepwise deshielding of the second methyl group. A similar observation has been made in the spectra of benzamides.[5] A reasonable explanation of this phenomenon may be found in the conformation of the amide function with respect to the aromatic system which places the second methyl group in the deshielding zone of the ring currents exerted by the π-electron cloud. In this connection, the pmr spectrum of 2,4,6-tri-*tert*-butyl-*N*,*N*-dimethylbenzamide is most noteworthy.[7] The methyl protons of the amide function of this compound resonate at δ 2.64 and 2.96. This indicates that one of the methyls is being largely shielded while the other methyl is unaffected. Owing to the extreme crowding in this case, the conformation of the amide function may be quite different, which places the second methyl out of the deshielding zone of the aromatic ring.

If the above arguments are valid, then the upfield methyl must be trans and the downfield methyl must be cis to the carbonyl group. It was necessary to obtain experimental evidence in support of this statement, as in the case of simple aliphatic amides the assignments made have been the opposite.[8] Recently, Lewin has demonstrated the use of the lanthanide chemical shift reagent, $Eu(DPM)_3$, to make such structural assignments to the protons of some tertiary amides.[9] It was found that the complexation of the metal by the lone pair of the carbonyl oxygen causes the resonance associated with the cis group to suffer a larger induced shift than the resonance of the anti group. The pmr spectra of all the amides in the present study were examined after a gradual addition of $Eu(DPM)_3$ in carbon tetrachloride solution. Up to molar ratios of approximately 0.8 [$Eu(DPM)_3$/substrate] the relationship between the induced downfield shifts and the moles of the reagent was essentially linear. The values obtained for the induced shifts of the two methyl signals at reagent/substrate molar ratio of 0.3 are presented in Table I. The data show that in all cases the downfield signal suffered a larger induced shift than the upfield signal. In addition, the signal exhibiting greater shift sensitivity also broadened to a larger extent. These results indicate that the upfield signal can be assigned to the trans methyl and the downfield to the cis methyl, thus proving the assignments made above to be correct.

Experimental Section

All the amides were prepared from the commercially available carboxylic acids by the following reaction sequence.

$$ArCOOH \xrightarrow{SOCl_2} ArCOCl \xrightarrow{NH(CH_3)_2} ArCON(CH_3)_2$$

The general procedure was similar to that employed by Meltzer, *et al.*, for the synthesis of *N*,*N*-dimethylisonicotinamide.[10] Amides **1**, **3**, and **5** were prepared in 80–90% yield while the yields of amides **2**, **4**, and **6** were considerably lower,

(7) H. A. Staab and D. Lauer, *Chem. Ber.*, **101**, 864 (1968).
(8) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, 253 (1960).
(9) A. H. Lewin, *Tetrahedron Lett.*, 3583 (1971).
(10) R. I. Meltzer, A. D. Lewis, and J. A. King, *J. Amer. Chem. Soc.*, **77**, 4062 (1955).

40–50%. Their ir, pmr, mass spectra, and elemental analysis (within 0.3% for C, H, and N) provided sufficient evidence for the correct structure and purity. The 60-MHz spectra of 0.5 *M* solutions in $CDCl_3$ were studied in degassed sealed tubes between the temperatures of 40 and 95°. The spectra were obtained on a Varian A-60A spectrometer. Temperatures were calibrated with ethylene glycol according to established procedures.[2]

Registry No.—**2**, 1903-64-6; **3**, 3815-24-5; **4**, 30721-92-7; **5**, 38308-87-1; **6**, 38308-88-2.

The Synthesis of 3,5-Dicarbethoxy-1,2,4-cyclopentanetrione. A Correction

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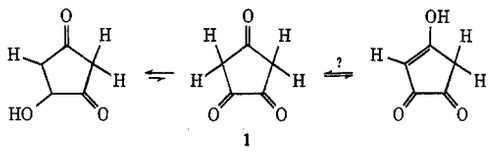
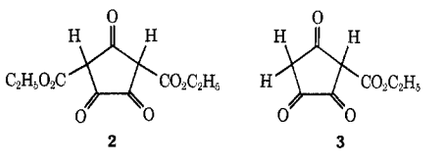
In connection with other work, we required 1,2,4-cyclopentanetrione (**1**), a material of some theoretical interest.[1] A convenient synthesis of **1** from 3,5-di-



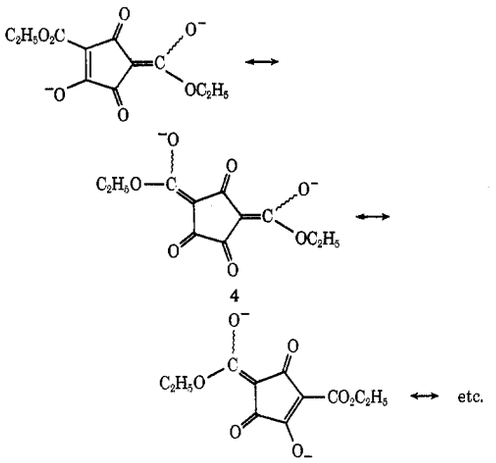
1

carbethoxy-1,2,4-cyclopentanetrione (**2**) has been reported.[2] In attempting to prepare **2**,[2-4] however, we encountered some experimental difficulty. In this process we have isolated and characterized 3,5-dicarbethoxy-1,2,4-cyclopentanetrione (**2**), an interesting and relatively unstable material with properties that differ considerably from those previously reported.[2-4] Furthermore, we would like to suggest that the properties previously reported for the title compound, **2**,[2-4] appear to best fit those for 3-carbethoxy-1,2,4-cyclopentanetrione (**3**), a hydrolysis product of **2**.



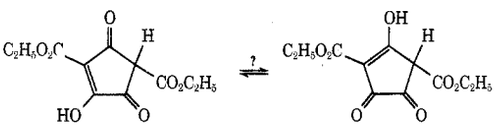
2 **3**

Treatment of diethyl acetonedicarboxylate, ethyl oxalate, and sodium or potassium ethoxide as reported[2,4] afforded a yellow salt which, following hydrolysis, could be converted to a viscous material which slowly crystallized. Trituration with a small amount of anhydrous ether gave **2** as a crude yellow solid. Recrystallization from anhydrous ether at 0° gave pure **2**, mp 107–109° dec. The nmr spectrum contained absorptions consistent with two nonequivalent ethoxy groups and a single methine hydrogen. The mass spectrum contained a parent peak at *m/e* 256 (calcd, 256). A neutralization equivalent of 127 (calcd, 128) was obtained by potentiometric titration. Two end points were clearly observable, with pK_a values of 2.1 and 5, estimated from the titration curve. In view of the similar enolic behavior of acylcyclopentanetriones[1c,5a] and related substances,[5b] the structure of this bis sodium or potassium salt, **4**, appears to be best represented as the following resonance hybrid.



4

The nmr spectrum of **4** in D_2O consisted of a single ethoxy resonance. Acidification of **4** regenerated the nmr spectrum of **2**, which appears to exist mainly in the diketone form **5** both in deuteriochloroform and in the solid phase (see Experimental Section).



5

In ethyl acetate, **2** readily dissolved and, upon standing, the solution darkened and a crystalline solid precipitated out, mp 145–147°. This new material, compound **3**, appears to be the material previously identified as the title compound.[2-4,6] The nmr and infrared spectra of this substance (**3**), which was isolated earlier by Wislicenus and Schöllkopf,[7] differs considerably from those of **2**. The nmr spectrum in acetone-d_6 consisted of a triplet and a quartet, characteristic of a single ethoxy group, and a singlet methine resonance which integrated as two protons, consistent with the enol form, **6**. In wet dimethyl-d_6 sulfoxide, two ethoxy resonances and a vinyl hydrogen were observed, suggesting an equilibrium between **6** and **7** or possibly **8** in this solvent. Compound **3** titrated (to a pH of 7) as a monoprotic acid, pK_a = 2.1, neut equiv 186 (calcd, 184). The mass spectrum of this material

(1) (a) C. F. Sheley and H. Schechter, *J. Org. Chem.*, **35**, 2367 (1970); (b) C. H. Depuy and E. F. Zaweski, *J. Amer. Chem. Soc.*, **79**, 3923 (1957); C. H. DePuy and E. F. Zaweski, *ibid.*, **81**, 4920 (1959); C. H. Depuy and P. R. Wells, *ibid.*, **82**, 2909 (1960); (c) K. Hiraga, *Chem. Pharm. Bull.*, **13**, 1300 (1965).

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(3) v. P. Ruggli and K. Doebel, *Helv. Chim. Acta*, **29**, 600 (1946).

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(5) (a) J. A. Elvidge and R. Stevens, *J. Chem. Soc.*, 2251 (1965); (b) S. Forsen and M. Nilsson in "Chemistry of the Carbonyl Group," Vol. 2, J. Zabicky, Ed., Interscience, New York, N. Y., 1970, p 157.

(6) We would like to thank Dr. R. G. Wilkinson[2] for kindly providing an infrared spectrum (solid phase) which confirmed the identity of the two materials.

(7) W. Wislicenus and K. Schollkopf, *J. Prakt. Chem.*, **95**, 269 (1917).