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Citation: The Journal of Chemical Physics **46**, 3132 (1967); doi: 10.1063/1.1841184
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Conformation and Internal Rotation of Nitroaromatic Amines in Solution as Detected by Proton Magnetic Resonance. II. Polynitro Acetanilides*

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(Received 7 November 1966)

The proton NMR spectra of several *N*-acetyl-*N*-methyl polynitroanilines reveal the presence of two conformers. The conformer ratio has been studied for the picrylaniline in various solvents, and the rate of conformer interchange for this substance was measured in 1,4-dioxane. Chemical-shift studies of these and various related molecules have given additional information about the configuration of these molecules. It is concluded that the acetamide group is normal to the plane of the aromatic ring for the *N*-acetyl-*N*-methyl-2,4,6-trinitro and 2,6-dinitro anilines.

I. INTRODUCTION

During a study of the conformation and internal rotation of various nitroaromatic amines in solution,[1] it was observed that the hydrogen peaks in the NMR spectra of *N*-acetyl-*N*-methyl-2,4,6-trinitroaniline (≡AM246), of *N*-acetyl-*N*-methyl-2,4-dinitroaniline (≡AM24), and of *N*-acetyl-*N*-methyl-2,6-dinitroaniline (≡AM26) are doublets. This observation can be satisfactorily explained in terms of two conformer species α and β; here α denotes the species more abundant at 25°C. Discussion of the relevant literature and details of the model for the conformers is, for convenience, deferred to a later section of this paper.

II. EXPERIMENTAL

Most of the NMR studies were carried out with a Varian A-60 (60.005 Mc/sec) spectrometer equipped with a V-6031 variable temperature probe. Some spectra were taken at 100 Mc/sec (Varian HA100) to confirm chemical shifts, and to study peaks from compounds with low solubility. A calibrated copper–constantan thermocouple was used to determine sample temperatures in the A-60 probe to ±0.5°. Most samples were studied in sealed degassed glass tubes. The 1,4-dioxane and benzene were distilled three times over sodium; the perdeutero acetone and d_8-dioxane (Volk, 99.5%) were used as received, as were the glacial (99.7%) acetic acid and concentrated (95.7%) sulfuric acid; the methylene chloride was distilled twice over P_2O_5 and then twice over dried K_2CO_3; the pyridine was distilled after drying over KOH. The room-temperature solubility of AM246 was about 0.7M in dioxane, 0.9*M* in acetone, and 0.5*M* in methylene chloride. Presence of 5–10% TMS in some of the samples did not perceptibly change the line positions and shapes of the spectral peaks. Absorption areas were obtained from the curves, taken at rf power levels sufficiently low to prevent saturation, by integration with a planimeter (A. Ott, Type 131 L).

The AM246 was prepared[2] by condensation of 7.5 g of methylamine hydrochloride and 25 g of picryl chloride in ethanol, in the presence of $NaHCO_3$. After refluxing two hours, the red solution yielded 16.3 g of yellow *N*-methyl-2,4,6-trinitroaniline crystals (≡HM246, m.p. 117° after recrystallization from ethanol). This picramide (15 g) was dissolved in acetic anhydride and a few drops of concentrated H_2SO_4 were added. After standing for 15 min, the pale-yellow solution was poured on ice. A yellow oil formed which solidified, after much scratching, into crystals which were filtered and washed with water. After recrystallization from ethanol, the crystals (14 g) were nearly white and melted at 129°. (Elemental analysis of AM246: found C—37.99, H—2.95, N—19.04; theoretical C—38.04, H—2.84, N—19.72.) Five subsequent recrystallizations, as well as attempts to remove impurities by chromatography using columns of acidic and basic alumina, did not affect the melting point or the NMR spectrum of the compound.

The *N*-methyl-*N*-perdeuteroacetyl-2,4,6-trinitroaniline (≡d_3-AM246) was prepared in the same way, except that CD_3COCl (obtained from CD_3CO_2H, Volk 99%) was substituted for the acetic anhydride. The pale-yellow crystals of d_3-AM246 melted at 129°.

The *N*-acetyl-*N*-methyl-2,4-dinitroaniline (≡AM24)[3] was prepared from *N*-methyl-2,4-dinitroaniline (≡HM24) in acetic anhydride containing a little sulfuric acid, m.p. 77°–78°C (elemental analysis of AM24: found C—45.26, H—3.77, N—17.75; theoretical C—45.19, H—3.79, N—17.57).

The *N*-acetyl-*N*-methyl-2,6-dinitroaniline (≡AM26) synthesis was carried out in an analogous fashion from 2,6-dinitro-chlorobenzene, giving a faintly yellow product melting at 125° (found C—45.22, H—3.91, N—17.08; theoretical C—45.19, H—3.79, N—17.57). This compound does not appear to have been previously described in the literature.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

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[3] M. M. de Monchy, Rec. Trav. Chim. **52**, 833 (1933).

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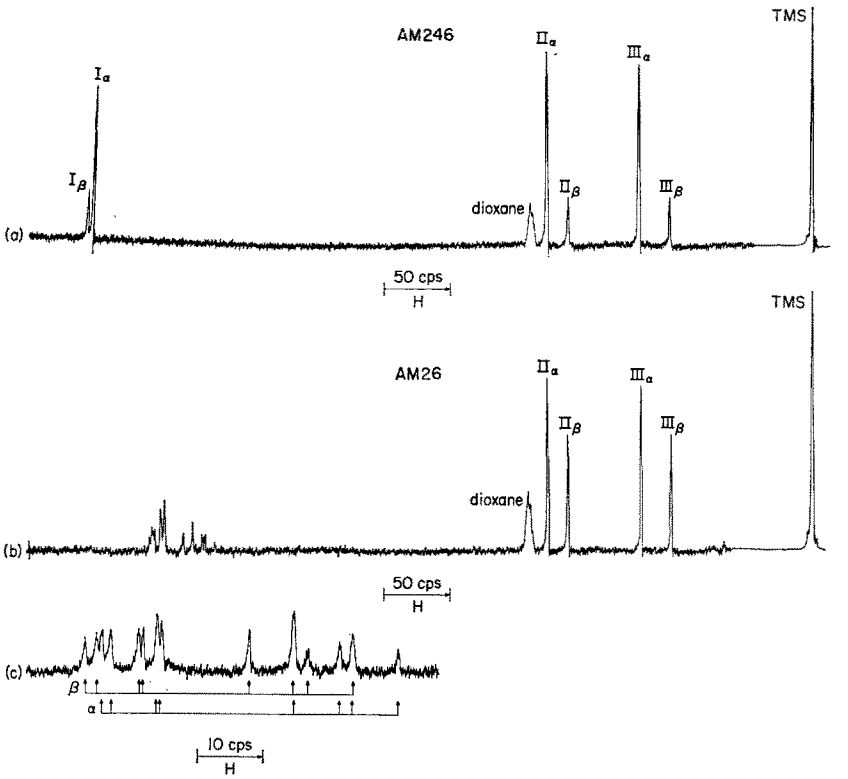

FIG. 1. The proton magnetic resonance spectra (60.005 Mc/sec and ~30°C) in d_8-1,4-dioxane of (a) AM246, (b) and (c) AM26: Here (c) is an expanded version of the A_2B part of spectrum (b). Peaks I arise from the picryl protons, Peaks II from the CH_3–N, and III from the CH_3CO groups.

The *N*-acetyl-2,4-dinitroaniline (≡AH24) was prepared from 2,4-dinitroaniline, just as described above, and melted at 121°C[4] (found C—42.87, H—3.25, N—18.22; theoretical C—42.67, H—3.13, N—18.66). The *N*-acetyl-2,4,6-trinitroaniline (≡AH246) was prepared using the method of Borsche,[5] giving crystals melting at 238.5°C (found: C—35.89, H—2.41, N—20.82; theoretical: C—35.57, H—2.24, N—20.74).

The 2,4-dinitroaniline (≡HH24), *N*-methyl-2,4-dinitroaniline (HM24), *N*,*N*-dimethyl-2,4-dinitroaniline (≡MM24), 2,4,6-trinitroaniline (≡HH246), and *N*,*N*-dimethyl-2,4,6-trinitroaniline (≡MM246) were prepared as described elsewhere.[1]

III. RESULTS

A. General Spectroscopic Features

The NMR spectrum of AM246 in d_8-1,4-dioxane is included in Fig. 1. The assignment of Peaks I_α and I_β to the picryl hydrogen atoms of Conformers α and β is based upon comparison of their absorption areas with those of the corresponding methyl peaks and the location of picryl peaks in similar compounds.[1] Peaks II_α and II_β are due to the *N*-methyl protons, whereas III_α and III_β arise from the acetyl methyl protons. These identifications are based upon the NMR spectrum of the analogous compound (d_3-AM246) containing a fully deuterated acetyl methyl group, and are consistent with the spectra of known polynitroaniline derivatives.[1] The relative area ratios $A_I:A_{II}:A_{III}$ for both species were within experimental error of the expected 2:3:3.

The α–β splitting of the picryl peaks of AM246 in the various alkyl halide solvents studied is only observable at lower temperatures and not at room temperature, whereas the methyl peaks clearly show the presence of both α and β conformers throughout the range studied. In oxygenic solvents, picryl α–β doublets are observable with the following splittings at 33°C: cyclohexanone 8 cps; d_6-acetone 7 cps; acetic anhydride 7 cps; pentanedione 4.5 cps; 1,4-dioxane 3.5 cps. The α–β chemical shifts (in the same order of solvents) increase from 13 to 19 cps for Peaks II and are about 23 cps for Peaks III in all the solvents studied except benzene, pyridine, and H_2SO_4. Table I includes the proton peak positions for AM246 in various solvents (accuracy ±0.3 cps).

The proton NMR spectrum of AM24 and AM26 also shows doubling of all peaks because of the presence of α and β forms, exactly analogous to the AM246 case, except that the aromatic ring protons give three-proton spectra; the A_2B spectra of AM26 conformers in dioxane are included in Fig. 1. Peak coalescence (≡disappearance of minimum between peaks) due to interchange of the α–β conformations occurs, for the acetyl methyl absorptions of the three compounds in

[4] W. Borsche, Ber. **50**, 1355 (1917).
[5] W. Borsche, Ber. **56**, 1939 (1923).

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TABLE I. Line positions ν at 25°C and their temperature dependence $\Delta\nu/\Delta T$, as well as the shifts $\delta\nu_{\alpha-\beta}$, in the NMR spectra of AM246 taken at 60.005 Mc/sec. Positive values of ν denote downfield shifts away from $Si(CH_3)_4$ used as internal standard; such shifts with increasing temperature are given by positive values of $\Delta\nu/\Delta T$. For 1,4-dioxane, $\nu=213.4$ cps at 25°C.

Compound	Solvent and temperature range	ν (cps), $\Delta\nu/\Delta T$ (cps/deg) in parentheses, and $\delta\nu_{\alpha-\beta}$ (cps)								
		I_α	I_β	$\delta\nu_{\alpha-\beta}$	II_α	II_β	$\delta\nu_{\alpha-\beta}$	III_α	III_β	$\delta\nu_{\alpha-\beta}$
AM246	Acetic acid, glacial (10°–52°)	542.9 (−0.024)	547.0 (−0.061)	−4.2	204.9 (−0.017)	190.6 (−0.010)	14.4	139 ...	118 ...	23
	d_6-Acetone (−7.5°–51°)	544.7 (−0.055)	552.4 (−0.087)	−7.7	205.5 (−0.017)		19.3	132.8 (−0.026)	110.6 (-0.009_5)	22.2
	Benzene (5°–51°)	473.4 (0.081)	(∼473.4)	∼0	152.2 (0.144)	167.4 (0.033)	−15.2	92.3 (0.083)	90.8 (−0.005)	1.5
	1,4-Dioxane	541.6	545.3	−3.7	...	...		129.8	106.9	22.9
	d_8-1,4-Dioxane (11.5°–41°)	541.5 (−0.052)	545.3 (−0.079)	−3.8	199.2 (−0.005)	183.1 (0.029)	16.1	129.8 (−0.014)	106.8 (0.000_6)	23.0
	Methylene chloride (−43°–32°)	539.1 (−0.080)	539.6 (−0.090)	−0.5	202.2 (−0.027)	187.4 (−0.021)	14.8	133.2 (−0.042)	110.6 (−0.035)	22.6
	Pyridine (10°–62°)	550.5 (−0.134)	565.7 (−0.207)	−15.2	199.8 (−0.028)	190.3 (−0.015)	9.5	127.5 (−0.007)	114.4 (−0.032)	13.1
	Sulfuric acid (95.7%)	$536._6$		...	$199._1$		...	$146._1$		...
d_8-AM246	d_8-1,4-Dioxane (18.5°–41°)	541.4 (−0.049)	545.2 (−0.097)	−3.8	199.1 (−0.003)	183.1 (0.029)	16.0	...	...	...

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dioxane at 60 Mc/sec, at the following temperatures: AM246 at 80°C, AM24 at 26°C, and AM26 at $T>95$°C.

The nmr spectrum of AM246 (and also the dinitroanilines) in benzene differs somewhat from that in nonaromatic solvents in that all peaks are shifted upfield relative to TMS, with the I and III doublets collapsed to single lines at room temperature. However, the methyl II peaks do exhibit α–β doubling (Table I), and the methyl III peaks also show such splitting at low temperatures (~5°C) or when measured at 100 Mc/sec. The identification of the II peaks was checked with d_3-AM246. Runs made in mixed dioxane–benzene solutions furnished the correlation between peaks α (and β) for pure benzene and pure dioxane.

In pyridine, AM246 shows α, β doubling of all three peaks (Table I); these coalesce in the range 60°–80°C. The picryl peaks are both shifted downfield, whereas the methyl absorptions occur more or less as in other solvents.

The AM246 is soluble in concentrated H_2SO_4 (95.7%; used as received) and exhibits only single I, II, and III peaks (Table I) somewhat broader than the analogous peaks in other solvents at the same concentration and temperature. The width of all lines decreases somewhat as the temperature is raised. However, there is increasingly rapid decomposition ($t_{1/2}$~5 h at 35°C) to acetic acid and *N*-methyl-2,4,6-trinitroaniline (as identified from NMR spectra of both, and isolation of the latter). In glacial acetic acid (99.7%), α–β splittings of all three peaks (I, II, III) are observed (Table I). As sulfuric acid is added, the β peaks increase compared to the α peaks, suggesting that pure form β (presumably a protonated version thereof) exists in H_2SO_4. However, the measurements are difficult because of the line broadening as the concentration of H_2SO_4 increases; this broadening may be caused by protonation kinetics or by viscosity effects. In addition, the reproducibility of these spectra was not very satisfactory.

In all the solvents studied, both α methyl peaks were found to have exactly the same area, demonstrating the absence of enol isomers involving the acetyl group; the same held true for the β methyl peaks. Various attempts were also made to utilize possible keto–enol interconversion to deuterate the carbonyl methyl peaks (for example, by heating AM246 in glacial acetic acid and D_2O with a few drops H_2SO_4); however, no change in the relative areas of the methyl proton peaks was observable.

For comparison purposes, spectra of various 2,4-dinitro and 2,4,6-trinitroanilines (HH24, AH24, HM24, MM24, HH246, AH246, HM246, and MM246) were taken in 1,4-dioxane or d_8-1,4-dioxane at 25°C. The peak positions are included in Table II; none of these substances exhibit α–β doubling. HM246 in dioxane shows but a single picryl peak, indicating rapid interchange of its two conformations[1]; it shows doubling of the methyl peak due to spin–spin coupling with the amine proton, as does HM24.

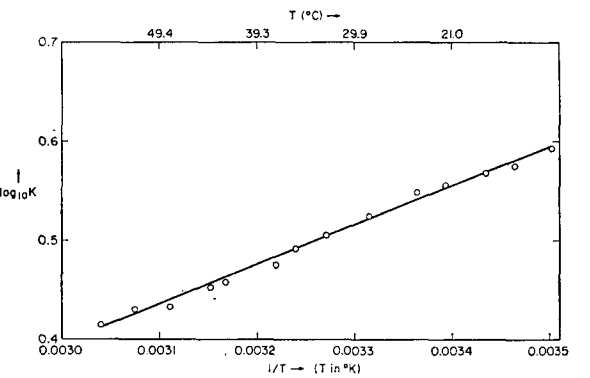

FIG. 2. The equilibrium constant K of AM246 conformers in d_8-1,4-dioxane as a function of temperature.

The infrared spectrum of AM246 in both dioxane and methylene chloride showed two barely resolved carbonyl stretching absorptions. The band at 1690 cm^{-1} was less intense than that at 1702 cm^{-1} and consequently was assigned to the β conformer.

B. Equilibrium Constants

The temperature dependence of the NMR spectra was studied in several solvents and yielded information about the equilibrium between the α and β forms. Detailed equilibrium and rate studies were made in 1,4-dioxane, since this solvent provides sufficiently high solubility of AM246 and offers a wide range of easily accessible temperatures encompassing the coalescence temperatures of all three doublets (at 60 Mc/sec: I—55°C, II—75°C, III—80°C).

Since Peak II_α falls very close to the solvent peak, it was found desirable to use fully deuterated dioxane. The equilibrium constant $K=A_{\alpha i}/A_{\beta i}$ (where i=I, II, III) was obtained at various temperatures from the ratio of the absorption areas and was found to be independent of the index i. Broadening of the peaks due to the kinetic effects caused an upper limit of 56°C for these measurements in dioxane. The averages of results obtained from all three peaks are presented in Table III. From the plot of $\log_{10}K$ vs $1/T$ (Fig. 2), the enthalpy and entropy of the reaction $\beta\rightarrow\alpha$ of AM246 were determined (Table IV). The effect of substituting deuterated solvent for ordinary dioxane was found to be negligible.

Similar measurements of K for AM246 in acetic acid, acetone, benzene, methylene chloride, and pyridine (Table III) yielded reaction enthalpies and entropies included in Table IV. The equilibrium constants for AM26 in d_8-1,4-dioxane are listed in Table III, and yielded values of ΔH and ΔS in Table IV. Only few values of K for AM24 in d_8-1,4-dioxane were measurable (Table III), because of its low peak coalescence temperature.

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TABLE II. Line positions (ν) in the NMR spectra of various polynitroanilines, taken at 60.005 Mc/sec in d_8-1,4-dioxane. Positive values of ν denote downfield shifts away from $Si(CH_3)_4$, used as internal standard. Values of line positions obtained by removing spin–spin splittings are included in parentheses.

Compound	T (°C)	ν (cps) Phenyl region [ring position of proton]			>N—CH₃	—CO—CH₃	>N—H
AM24	12.5	α overlapping broad peaks α 503–529 α 453, 462 (broad)	[3] [5] [6]		α 211.0 β 188.2	α 130.6 β 106.2	... ...
		β overlapping broad peaks β 503–529 β(460), 469 (broad)	[3] [5] [6]				
	25.4	524 (broad) 505, 508, 513, 516 455, 464 (broad)	[3] [5] [6]	(~524) (510.5) (459.5)	α 210 (broad) β 192 (broad)	α 129 (broad) β 108 (broad)	...
	51.4	524.9, 527.4 504.3, 506.8, 512.8, 515.6 454.9, 463.5	[3] [5] [6]	(526.2) (509.9) (459.2)	199.1	119.5	...
AM26	25.3	α 488.6, 489.3, 496.4, 497.8 α 451.3, 458.5, 460.3,[a] 467.7 β 491.4, 492.1, 498.9, 500.8 β 458.5, 465.5, 467.7,[a] 474.6	[3, 5] [4] [3, 5] [4]	(492.3) (460.3) (494.9) (467.7)	α 198.3 β 183.4	α 128.6 β 105.8	... ...
AH24	24.8	538.1, 540.7 500.8, 503.4, 510.1, 512.7[b] 531.4, 540.7	[3] [5] [6]	(539.4) (506.8) (536.0)	...	137.0	620 (broad)
AH246	25.0	543.6	[3, 5]		...	131.7	593 (broad)
HM24	25.3	539.9, 542.5 490.0, 492.6, 499.5, 502.2[c] 413.5, 423.0	[3] [5] [6]	(541.2) (496.1) (418.3)	181.3, 186.4 (183.9)	...	510 (broad)
HM246	25.3	540.0	[3, 5]		172.6, 178.1 (175.3)	...	535 (broad)
MM24	25.4	512.5, 515.2 482.3, 485.0, 491.7, 494.2 420.2, 429.8	[3] [5] [6]	(513.8) (488.3) (425.0)	181.0	...	...
MM246	25.1	525.5	[3, 5]		174.7	...	...
HH24	25	537.4, 540.0 483.2, 485.8, 492.6, 495.2 406.0, 415.4	[3] [5] [6]	(538.7) (489.2) (410.7)	...	...	442 (broad)
HH246	24.9	555.0	[3, 5]		...	...	532 (broad)

[a] Antisymmetric transition, see Ref. 9. [b] Additional splitting of ~0.3 cps in each peak. [c] Additional splitting of 0.7 cps in each peak.

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TABLE III. The equilibrium constant $K=P_\alpha/P_\beta$ at various temperatures, for AM246 in several solvents, AM24 and AM26 in d_8-1,4-dioxane.

Solute	Solvent	Temperature	K	Solvent	Temperature	K
AM246	d_8-1,4-Dioxane	12.0°C	3.92	Pyridine	−15.3°C	3.28
		15.5	3.76		0.7	3.02
		18.0	3.70		25.1	2.64
		21.5	3.59		37.5	2.52
		24.0	3.53		50.0	2.41
		28.5	3.34		61.7	2.295
		32.5	3.21			
		35.5	3.10	d_6-Acetone	−7.50	3.025
		37.5	2.99		4.75	2.73
		42.5	2.87		35.0	2.015
		44.0	2.84		51.0	1.80
		48.0	2.71			
		52.0	2.70	Methylene chloride		
		56.0	2.60		0.0	5.51
					9.75	4.82
	1,4-Dioxane	35.5	3.11		31.0	3.34
	Acetic acid	9.8	2.39	Benzene	5.0	7.19
		18.2	2.30		9.75	6.585
		25.2	2.22		24.0	5.35
		37.0	2.12		32.0	4.90
		50.5	1.99		51.0	3.80
AM24	d_8-1,4-dioxane	12.9	1.84			
		18.4	1.73			
AM26	d_8-1,4-dioxane	12.7$_5$	1.55			
		21.5	1.47			
		31.0	1.36			
		39.0	1.28			
		50.2	1.19			

C. Interconversion of the Conformers

Since coalescence of the α–β doublets was observable, it was possible to perform kinetic studies of the interchange between the two conformers. Onset of coalescence was accompanied by considerable line broadening, with relatively slight change in the spacing of the peaks.

The mean lifetimes τ_α and τ_β of the AM246 conformers in 1,4-dioxane were determined at many temperatures in the range 48°–100°C by fitting the experimental NMR line shapes to the theoretical line shape:

$$v(\Delta\omega)=C\,\frac{\{1+\tau[(P_\beta/T_{2\alpha})+(P_\alpha/T_{2\beta})]\}P+\tau[\Delta\omega-\tfrac{1}{2}\delta\omega(P_\alpha-P_\beta)]R}{P^2+R^2} \tag{1}$$

derived for an asymmetric doublet[6,7] centered at $\Delta\omega=0$. Here $\tau^{-1}=\tau_\alpha^{-1}+\tau_\beta^{-1}$, with $P_\alpha\tau_\alpha^{-1}=P_\beta\tau_\beta^{-1}$ under equilibrium conditions, and

$$P=\tau[(1/T_{2\alpha}T_{2\beta})-(\Delta\omega)^2+(\tfrac{1}{2}\delta\omega)^2]+(P_\alpha/T_{2\alpha})+(P_\beta/T_{2\beta}), \tag{1a}$$

$$R=\Delta\omega\{1+\tau[(1/T_{2\alpha})+(1/T_{2\beta})]\}+\tfrac{1}{2}\delta\omega\{\tau[(1/T_{2\beta})-(1/T_{2\alpha})]+(P_\alpha-P_\beta)\}. \tag{1b}$$

The fractional populations P_α and $P_\beta=1-P_\alpha$ at each temperature were obtained from extrapolation of the equilibrium constant $K=P_\alpha/P_\beta$ (Tables III and IV). The chemical shifts $\delta\nu_{\alpha-\beta}$ $(=\delta\omega/2\pi)$ of the doublets were derived from the data of Table I and are listed in Table V. The values of the transverse relaxation time $T_{2\alpha}$ and $T_{2\beta}$ are listed in Table V and were obtained from the limiting value of the full linewidth W at half-height as the temperature was lowered from the coalescence region, by use of the relation $T_2=(\pi W)^{-1}$. The values of $T_{2\alpha}$ and $T_{2\beta}$ did not sensitively affect the lineshapes in the regions of interest. The line shapes (1) were generated by an IBM 1620 computer with a 1627 plotter. Use of the parameters in Table V, along with the correct relative intensity of the doublet as obtained from K, yielded excellent agreement between the experimental spectra of the picryl protons and the lines calculated from (1). The resulting τ values are given in Table V. An Arrhenius plot log τ^{-1} vs $1/T$ (Fig. 3) yielded a good straight-line fit.

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

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TABLE IV. The temperature dependence $\log_{10}K=x+yT^{-1}$; enthalpy and entropy of the reaction $\beta\rightarrow\alpha$ for AM246 and AM26.

Solute	Solvent	x	y (°K)	ΔH (kcal/mole)	ΔS (eu)
AM246	Acetic acid	−0.218±0.046	168±14	−0.77±0.06	−1.00±0.21
	d_6-Acetone	−0.790±0.034	339±10	−1.55±0.05	-3.61_5±0.16
	Benzene	−1.083±0.037	540±11	−2.47±0.05	-4.95_5±0.17
	d_8-1,4-Dioxane	−0.796±0.029	397±9	−1.82±0.04	−3.64±0.14
	Methylene chloride	−1.529±0.035	624±10	−2.86±0.05	−6.99±0.16
	Pyridine	−0.153±0.007	172±2	−0.79±0.01	−0.70±0.03
AM26	d_8-1,4-Dioxane	−0.808±0.031	286±9	−1.31±0.04	−3.70±0.14

When attempts were made to fit the methyl peaks using Formula (1), values of τ in approximate agreement with (but slightly larger than) those from the picryl peaks were obtained below the coalescence temperature, with increasing difficulty in fitting the spectra at increasing temperatures. On the other hand, attempts to fit the II methyl peaks of *N*-methyl, *N*-perdeuteroacetyl-2,4,6-trinitroaniline in d_8-1,4-dioxane gave excellent results throughout the whole temperature region, yielding τ values (Table V) in good agreement with those obtained from the picryl peaks, as shown in Fig. 3. Lifetimes τ measured from the picryl peaks I of d_3-AM246 also agreed with those from ordinary AM246.

From the best-fitting line through the points in Table V and Fig. 3, energies of activation and frequency factors were calculated for the picryl points, for the methyl-II points, and for both of these sets combined. These are presented in Table VI. Similar calculations were carried out (Table VI) with the mean lifetimes τ_α and τ_β of the individual conformers α and β, respectively, obtained from τ and K at each temperature.

Most probably, the better fits obtained with the deuterated AM246 result from the decreased spin–spin interaction between the methyl groups in this compound. Concomitant with this, it was found that the widths of the II-methyl peaks in the deuterated AM246 were somewhat less than in ordinary AM246. It was also noted that the widths of the β peaks were appreciably greater than the widths of the corresponding α peaks for both methyl groups of AM246 in d_8-dioxane at 20°C.

TABLE V. The conformer lifetimes τ of AM246 as a function of temperature, in d_8-1,4-dioxane.

T (°C)	τ (sec) from picryl peak of AM246[a]	T (°C)	τ (sec) from *N*-methyl peak of d_3-AM246[b]
48.0	0.27		
52.0	0.18	56.0	0.110
56.0	0.11_2	64.0	0.060
61.5	0.079	69.0	0.041
64.5	0.057	72.0	0.030
68.0	0.041	76.0	0.023
70.0	0.034	80.5	0.017
72.5	0.028	88.0	0.0080
74.0	0.022_5	94.0	0.0054
75.5	0.021		
79.5	0.017		
82.0	0.012_5		

[a] Fitted using: $\delta\nu_{\alpha\text{-}\beta}=-3.20$ cps; $T_{2\alpha}=0.63$ sec; $T_{2\beta}=0.68$ sec.
[b] Fitted using: $\delta\nu_{\alpha\text{-}\beta}=15.60$ cps; $T_{2\alpha}=0.53$ sec; $T_{2\beta}=0.38$ sec.

D. Aggregation Studies

To investigate the possibility that the phenomena observed were dependent upon the state of aggregation of the AM246 molecules in solution, freezing-point-depression studies were carried out. Using usual methods,[8] AM246 was found (Table VII) to be monomeric in 1,4-dioxane and in benzene, purified in the same manner as when these solvents were used for NMR spectra. This result was obtained at various solute concentrations, including the ones used for the NMR experiments. We can calculate the equilibrium constant $K=P_\alpha/P_\beta$ at the freezing point for these two solvents from Table III. We note that if β were a dimeric pair of solute molecules, rather than a conformer of α,

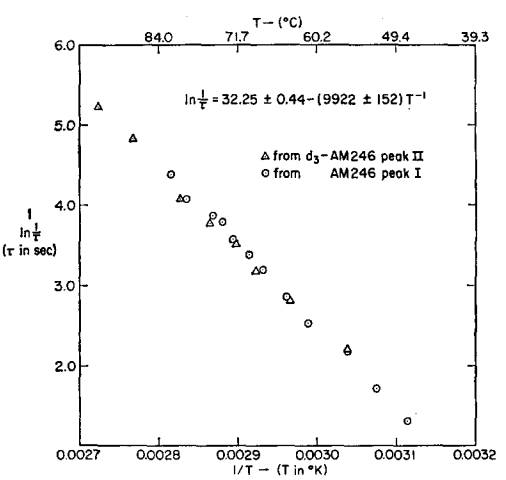

FIG. 3. The Arrhenius plot for the mean conformer lifetime τ of AM246 in d_8-1,4-dioxane.

[8] F. Daniels, J. H. Mathews, J. W. Williams, P. Bender, and R. A. Alberty, *Experimental Physical Chemistry* (McGraw-Hill Book Co., New York, 1956), 5th ed., pp. 65–71.

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we would expect apparent molecular weights $M_{app}=M_\alpha(P_\alpha+\frac{1}{2}P_\beta)^{-1}$ having values of 316 and 302 for dioxane and benzene, respectively. These are outside the limits of error of the observed values in Table VI. By analogous reasoning, we can rule out dissociation of AM246 molecules into two (or more) species.

E. Chemical Shifts and Coupling Constants

The peak positions of AH24 (Table II) lead to coupling constants for the aromatic protons of $J_{ortho}=9.3$ cps and $J_{meta}=2.6$ cps for 60-Mc/sec measurements in d_8-1,4-dioxane at 25°C. These parameters and the line positions were essentially the same at 12° and 50°C, as was the single methyl peak position and the NH absorption position. The corresponding data for HH24 yield: $J_{ortho}=9.5$ cps, $J_{meta}=2.5$ cps; and for HM24: $J_{ortho}=9.6$ cps, $J_{meta}=2.6$ cps and $J_{NH,NCH_3}=5.2$ cps. In CH_2Cl_2, the N–CH_3 peak shows a large downfield shift as the temperature is lowered[1]; at the lowest available temperature in d_8-1,4-dioxane (10.4°C), there was no difference in the position of the N–CN_3 doublet compared to 25°C. In MM24, $J_{ortho}=9.5$ cps, $J_{meta}=2.6$. The data for HH24, HM24, and MM24 are in good agreement with those in CH_2Cl_2.[1]

There exists an additional doublet splitting (0.7 cps) of each peak in the 5-proton quartet of HM24 in dioxane at room temperature, but not in the 3- or 6- proton doublets. The splitting is most easily observable, for sensitivity reasons, at 100 Mc/sec. Similarly, AH24 and 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine show analogous splittings of ~0.3 and 0.7 cps, respectively. No such splitting was observable in HM246 or AH246. Exchange of the NH hydrogen with deuterium removed the additional splitting, without affecting the 3- or 6-proton doublets. This demonstrates that there is long-range coupling between the amine proton and the phenyl proton *meta* to it. The extra splitting was not observable for AH24 in acetone.

We did not observe any splittings or width effects ascribable to nonzero values of J_{para} in any of the aromatic proton spectra.

TABLE VI. The energies of activation E_{act} (kilocalories per mole) and frequency factors A (per second) of the isomerization process for AM246 in d_8-dioxane.

	Peaks I	Peaks II	Peaks I+II
E_{act} (kcal/mole)	20.2±0.3	19.3±0.5	19.7±0.3
$\log_{10}A$ (A in sec^{-1})	14.4±0.2	13.7_5±0.3	14.0±0.2
E_{act}^{α} (kcal/mole)	21.5±0.4	20.5±0.5	21.0±0.3
$\log_{10}A^{\alpha}$ (A^{α} in sec^{-1})	14.7±0.2	14.0±0.3	14.3±0.2
E_{act}^{β} (kcal/mole)	19.7±0.3	18.7±0.5	19.2±0.3
$\log_{10}A^{\beta}$ (A^{β} in sec^{-1})	13.9±0.2	13.2±0.3	13.5±0.2

TABLE VII. The molecular weight of AM246 in dilute solution.

1,4-Dioxane		Benzene	
Molality of AM246 soln.	Apparent mol. wt of AM246[a]	Molality of AM246 soln.	Apparent mol. wt of AM246
0.024	285.2	0.0083	288.6
0.180	265.1	0.0107	284.3
0.267	278.2	0.0175	286.7
0.400	293.7	0.0230	279.5
0.620	289.4		

[a] Theoretical molecular weight of AM246=284.195.

The A_2B spectrum of the ring protons in AM26 (Fig. 1 and Table II) yielded chemical shifts $\delta\nu=\nu_{3,5}-\nu_4$ and *ortho* coupling constants determined[9] in d_8—1,4-dioxane at 30°C (60 Mc/sec) as follows: $\delta\nu_\alpha=32.0$, $J_\alpha=8.2_2$ and $\delta\nu_\beta=27.2$, $J_\beta=8.2_5$ (all in cps). These values were checked at 100 Mc/sec.

The temperature dependences of chemical shifts for AM246 in various solvents are included in Table I, and were obtained by linear fitting to the points. The accuracy in some cases was limited by small temperature variation coupled with the limits of accuracy (±0.3 cps) in measuring the shifts. At the lowest temperatures, deviations from linearity towards larger downfield shifts per degree of decreasing temperature were observed in pyridine ($T<10$°C).

IV. DISCUSSION

In the *N*-acetyl-*N*-methyl-nitroanilines investigated in this work, rotation about the carbon–nitrogen bond between the acetyl group and the amine nitrogen atom (≡N_1), as well as that about the carbon–nitrogen bond between the phenyl ring and N_1, is probably not free. Primary facts to be explained by a molecular model are:

(1) There exist two conformers α and β.

(2) The methyl NMR peak positions of α and β differ considerably, and much more than the picryl peak positions of α and β.

(3) The 3 and 5 phenyl protons act as equivalents in all our studies of these compounds, in contradistinction to those of HM246=N-methyl-2,4,6-trinitroaniline (which gives picryl splittings caused primarily by differences in the orientations of the two nitro groups ortho to the amine group).[1]

Two conformers, differing in the positions of the acetyl groups, suggest themselves from consideration of the possible bonding geometry and the stringent steric requirements in AM246 (and AM26). In these

[9] P. L. Corio, Chem. Rev. 60, 363 (1960).

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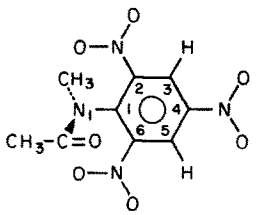
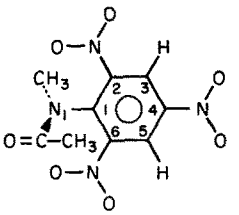
forms called A and B (shown below) the methyl groups

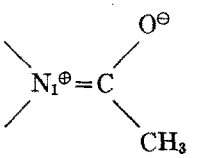


A – endo form



B – exo form

are *cis and trans* to each other, respectively. In both, the most important resonance structures are those placing positive charge on N_1 and negative charge on the carbonyl oxygen atom, with strong double-bond character for the amide bond



resulting in a barrier to rotation about this bond, as well as a tendency towards planarity of the bond system. In both forms, we take the plane containing the N_1–CH_3 and N_1–$COCH_3$ sigma bonds to be perpendicular to the plane of the aromatic ring, so that the acetamide π-electron system is effectively decoupled from the picryl π system. The three nitro groups are considered coplanar with the ring. Form A has the carbonyl group above C_1 of the ring (*endo* form) whereas in Form B, the carbonyl group projects out of the molecule (*exo* form) with the acetyl methyl group located above C_1. Thus, there is a plane of symmetry perpendicular to the ring and passing through Carbon Atoms C_1 and C_4 in both A and B. Existence of two such forms clearly can explain qualitatively all three primary observations (1), (2), and (3) listed above. The absence of observable enol forms also is consistent with well-developed double-bond character of the amide bond.

Because the proton NMR spectra[1] of HM246 indicate that rotation about N_1–C_1 is hindered and that the σ-bond system for N_1 is coplanar with the aromatic ring, one must also consider possible models for AM246 with similar geometry. In AM246, such a planar geometry would lead to steric interference, forcing both groups $(NO_2)_{2,6}$ out of the plane (however not necessarily by equal amounts). The steric effects in HM246 force only one of these nitro groups out of the plane, causing inequivalence of the ring protons $H_{3,5}$ detectable by NMR. In contrast, the picryl protons of AM246 appeared entirely equivalent in our NMR studies. There are differences between these protons of the α form and those of the β form, but within each comformer there is no observable difference between H_3 and H_5. Thus, one can conclude that in AM246 either (1) rotation about N_1–C_1 is essentially unhindered, or (2) rotation about N_1–C_1 is inhibited, but the resulting fixed orientation of the *N*-methyl and *N*-acetyl groups with respect to H_3 and H_5 produces no observable inequivalence between these protons. The former possibility seems most unlikely from consideration of space-filling Fisher–Hirshfelder–Taylor models, which show that such rotation is most difficult unless both $(NO_2)_{2,6}$ are perpendicular to the ring. This situation can be excluded not only from the energy considerations involved in rotating these nitro groups and the N_1 amine group but also, experimentally (Tables I and II), from the positions of $H_{3,5}$ NMR peaks, which are very sensitive[1] to the orientations of $(NO_2)_{2,6}$.

The second possibility presented above cannot explain why in AM246, unlike in HM246, there exist two distinct conformeric molecules. Thus, even if Form α or β of AM246 had the above-mentioned "coplanar" configuration, it would be necessary to involke a barrier to rotation about the amide linkage.

Moreover, in the coplanar model, steric interference would force the C–CH_3 and C=O groups to be situated in a plane perpendicular to the ring, so that the two species related by rotation by π about the amide bond would not be distinct. Hence, even if α or β had the coplanar configuration, the other observed conformer would necessarily be of the rotated-plane type, i.e., have its N_1 σ-bond system rotated away from the plane of the ring, and the question would immediately arise of why there should be only a single observable species of the latter type.

This situation could occur if the rotation about the amide bond is so strongly hindered that only one conformer exists, but it is difficult to see from free-energy considerations how a coplanar conformer, with little amide double-bond character, could co-exist with such a highly stable rotated-plane conformer. Furthermore, unsymmetrically N,N-disubstituted acetamides generally contain appreciable concentrations of both *cis* and *trans* isomers. In view also of the considerable circumstantial evidence from chemical shifts and trends in the equilibrium constants, to be discussed, we interpret our results in terms of the rotated-plane conformers A, B with the barrier to rotation about C_1–N_1 imposed only by steric considerations rather than double-bond character of C_1–N_1. In particular, the small α–β shifts of the picryl protons, compared to those of the methyl groups in most solvents, are not suggestive of major differences in the orientation of the nitro groups and in the π bonding of N_1 in the two observed isomers.

Considerable semiquantitative evidence for correlation of conformer α with Model A, and β with B, can be adduced, as follows: Several factors appear important in determining the relative energies of Forms A and B.

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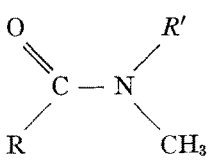
Since the nitro groups cannot effectively withdraw charge from N_1 in these forms, and since these groups cause C_1 to be relatively positive in charge, it seems reasonable that placement of the negative carbonyl oxygen atom above C_1 (i.e., Form A) will be favored. Interactions with solvent molecules may also favor this form, since it should be more polar than Form B. On the other hand, steric interference of the two methyl groups in A would act in the opposite direction, causing the enthalpy of the reaction to be relatively small and giving a sizable contribution to the entropy of reaction by hindering free rotation of the methyl groups. We note that $H_\alpha - H_\beta$ and $S_\alpha - S_\beta$ are both negative (Table IV). Unlike the situation in *N*-methylacetamide, where ΔH and ΔS are presumably of opposite sign and combine to make ΔF sufficiently large that only the conformer with the methyl groups *trans* to each other is observed,[6,10,11] in AM246 we find dominance at room temperature of Form A having the methyl groups *cis* to each other, with Form B predominating at sufficiently high temperatures.

Furthermore, in Form A, comparatively little shielding of the methyl groups by either the carbonyl group or the aromatic π system is to be expected, whereas in Form B one will expect more effective shielding of N_1–CH_3 (Line II) by the carbonyl group and of C–CH_3 (Line III) by the ring. The latter methyl group would be expected to show a larger α–β chemical shift, since its surroundings differ more in the two forms. These observations are all consistent with the assignment of Form A to Conformer α, as can be seen from Table I. This assignment is consistent with findings in *N*,*N*-dimethylacetamide and related *N*,*N*-disubstituted amides



that the N–CH_3 group *cis* to the carbonyl group is more shielded than the *trans* group.[12]

The relative positions of the picryl peaks (Lines I, Table I) of Forms α and β in AM246, with α more shielded than β, are also consistent with the model, in that the electron density on the picryl protons could well be expected to increase via shifts in the π-electron density due to the presence of the negative oxygen atom above C_1 in Form A. The picryl α–β shifts are also explainable if motion of the acetamide group causes the nitro groups *ortho* to C_1 to lie, on the average, slightly out of the plane of the ring in Form A, as a result of repulsion between the carbonyl and nitro oxygen atoms.

The widths of the methyl lines II_β and III_β are greater than those of the corresponding α lines, most probably as a result of spin–spin interaction ($J \sim$ 0.1–0.3 cps) between the methyl groups. Again, this is in concert with the identification of Forms A and B, in that *trans* coupling coefficients are known to be considerably larger than *cis* coupling coefficients in this type of compound.[13–15] It is, of course, likely that the double-bond character of C–N_1 is not exactly the same for the α and β forms.

In studies of unsymmetrically *N*,*N*-disubstituted acetamides, it has been established that the bulkier group attached to the nitrogen atom tends to be *cis* to the carbonyl oxygen[12]; this has been explained in terms of steric effects with the assumption that methyl is effectively larger than oxygen. Again, these ideas are consistent with our assignment of models.

Studies of N-acetyl-N-methylaniline (*N*-methylacetanilide) by electric-dipole measurements[16] and by NMR and x-ray structural analysis[17] have revealed that even in this far less sterically hindered molecule, there exist two conformers with the amide bond normal to the benzene ring. The molecules in the solid have the *exo* form, which is also dominant (99.5%) in pyridine solution. In crystalline acetanilide, it was found[18] that the amide group is planar (with its plane at an angle of 17.6° to the benzene ring), and linked by hydrogen bonding to its neighbors. For the molecules *N*-acetyl-2,6-diiodoaniline, as well as *N*-acetyl-*N*-methyl-2,6-diiodoaniline, the conformers can even be chemically separated and isolated[19]; the former occurs preferentially in the *endo* form, whereas the latter prefers the *exo* form (presumably because of methyl–methyl repulsion and lack of stabilization of the carbonyl oxygen above the ring).

The methyl peaks of *N*-methylacetanilide in pyridine[17] are, relative to $Si(CH_3)_4$, acetyl: *exo* 113 cps and endo 134; *N*-methyl: *exo* 195 and *endo* 193. These are quite similar to the shifts observed herein (Tables I and II) and confirm the correlation α=A (*endo*).

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It is well known that solvent effects and, in some cases, agregation of solute molecules greatly influence the barrier to rotation.[20–26] The freezing-point-lowering experiment (Sec. 3.D) shows that AM246 does not associate appreciably. Tables III and IV demonstrate that the equilibrium for AM246 is indeed influenced considerably by the solvent; however, ΔH and $T\Delta S$ tend to cancel and vary in the same way with solvent so that K is relatively constant. No solvent studies of the interconversion rates have been made.

It is probable that, in benzene, there exist labile "collision" complexes in which the π-electron system of benzene couples to the positively charged part(s) of the solute molecule.[21] In Form A, there clearly exists a methyl region more positive than the one in Form B, and this is again consistent with the identification $\alpha \leftrightarrow$A.

The distinctive chemical shifts upfield observed for formamides and acetamides in benzene have been discussed by Hatton and Richards[21] and evidence for complex formation was also adduced[24] from the temperature dependence of these shifts. For AM246 in benzene, we observe large chemical shifts upfield compared with nonaromatic solvents (Table I). These are particularly large for Conformer α, which also exhibits a much larger temperature dependence of the shifts than β (both shifts being of opposite sign to those in nonaromatic solvents, as was found in Ref. 24). The methyl peak II_α is more strongly perturbed than III_α, suggesting that the benzene molecule is associated with the N-methyl group; this is of course consistent with the tendency to attach near the positive amine nitrogen atom and away from the carbonyl group. LaPlanche and Rogers[11] found that the methyl group trans to the carbonyl oxygens shows a larger upfield shift on diluting with benzene than the methyl group *cis* to the carbonyl group; Table I shows that Peak II_α shows the largest such shift, once again consistent with the identification $\alpha \leftrightarrow$A.

It is known that amides in sulfuric acid are protonated on the carbonyl oxygen atom, with strong enhancement of the double-bond character of the amide linkage.[14,22,27,28] The picryl peak position of AM246 in this solvent is much like that in other solvents, so that it appears unlikely that protonation takes place on the nitro groups. Addition of a proton to the carbonyl group would presumably destabilize the *endo* form A, and the resulting stronger amide double bond could raise the barrier to rotation sufficiently to allow only the existence of one conformer, in the *exo* configuration. The enhanced double bond should cause the N–CH_3 and (to an even larger extent) the C–CH_3 peaks to be shifted to lower fields,[27] as is indeed the case (Table I). Similar trends in the shifts (and in K) are visible for AM246 in acetic acid.

In pyridine, our results suggest presence of weak complexing between AM246 and pyridine (Table I). Presumably, if the rings were adjacent, it would be possible to account for the downfield shift of the picryl proton peaks in terms of ring-current effects from the pyridine molecules. The larger shift for β indicates stronger complexing than in α, consistent with greater capability for accepting electron density by the ring in conformer β. For comparison, HM246 in pyridine at 25.1°C shows a broad N–H peak at 580 cps, a single picryl peak at 542.4 and a single CH_3 peak at 177.0; doubling of the latter peak due to the amine hydrogen becomes observable only at −15°C. This collapse of the methyl doublet may indicate rapid transfer of the amine proton to the pyridine; however, the CH_3 peak position is not abnormal in pyridine, as compared to other solvents.

The magnitude of the activation energy (Table VI) as well as of the frequency factor, for the conformer interchange of AM246 in dioxane, is reasonable for hindered rotations in N,N-disubstituted acetamides.[6,7,23,26,29] These parameters are thought to be rather complex functions of the molecular geometry and motions, and particularly sensitive to interactions with the solvent.[26]

From the equilibrium constants (Table III), it is evident that the percentage of α compared to β decreases in going from AM246 to AM24 to AM26. Presumably, steric effects affecting hindered rotation and the conformations α and β in AM246 and AM26 will be similar. Indeed, we note the great similarity of the methyl peak positions (Tables I, II) of the two compounds. The relative equilibrium constants are explicable by arguing that absence of the nitro group *para* to C_1 in AM26 causes C_1 to be comparatively less positive than in AM246, i.e., diminishing attraction between C_1 and the carbonyl group present above C_1 in Form A. This would also decrease any tendency for electron withdrawal from N_1 by the ring system, thereby enhancing the amide double-bond character and increasing the barrier to rotation about this bond. In fact, the coalescence temperatures for peaks of AM26 are higher than those of AM246.

From Table IV it is seen that ΔS of reaction for

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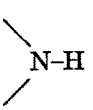
AM26 is about the same as that for AM246 (both in d_8-1,4-dioxane), whereas ΔH is appreciably lower. This is understandable on the basis of the (A, B) model if we assume that ΔS arises largely from the difference in freedom of methyl rotation in Forms A and B, which would be identical in AM26 and AM246. On the other hand, the difference in energy of Forms A and B would be smaller in AM26 if location of the carbonyl oxygen atom above C_1 is indeed an important factor.

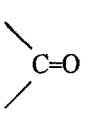
In contrast, the coalescence temperatures for the peaks of AM24 are lower. We note (Tables I, II) that the acetyl methyl peaks are close to those of AM246 and AM26, whereas the *N*-methyl peaks are shifted downfield by comparison. We can explain this by assuming deviations from perpendicularity of the amide and the aromatic system, i.e., greater double-bond character of C_1–N_1 and correspondingly less for the amide linkage. The N–CH_3 shift corresponds to decreased proximity of the *N*-methyl and nitro group *ortho* to C_1.[1]

In studies of certain *N*,*N*-disubstituted amides containing two different groups *ortho* to the aniline nitrogen atom, with α-methylene groups on the amide nitrogen atom, it was found[30] that the two methylene protons are inequivalent, but become equivalent at sufficiently high temperatures. This was ascribed to hindered rotation about the benzene–amine nitrogen bond. We have not investigated any NMR spectra of *N*-acetyl-*N*-ethyl-2,4-dinitroanilines, although these should be interesting.

The question of why AH24 and AH246 do not show isomer pairs is not yet answered completely satisfactorily. LaPlanche and Rogers[11] have shown that only very few N-substituted amides, exclusively formamides, occur as conformeric pairs. The conformation in which the

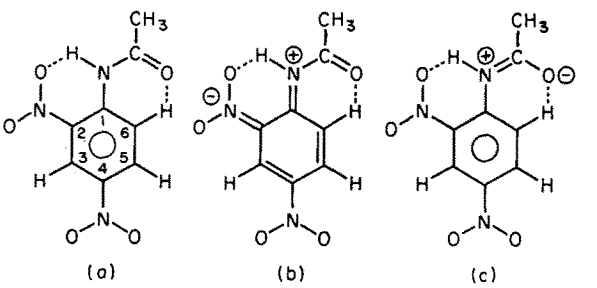


group is *trans* to



predominates. Comparison of the chemical shifts of the acetyl methyl group (Table II) for AH24 and AH246 with those of the AM compounds (i.e., Peaks III) suggests that the same is true here. Absence of methyl–methyl interference in the AH compounds would tend to stabilize the *endo* form of AH246, consistent with the above. It also seems possible, in the case of AH246, that solute association in chains, such as has been discussed by Mizushima[10] and LaPlanche, Thompson, and Rogers,[31] is an important factor.

However, in AH24, we observe evidence of internal hydrogen bonding.[32] We note from Table II that the H_6 peak in AH24 is shifted remarkably downfield compared to that of AM24, HM24, MM24, and HH24. Furthermore, the N–H absorption of AH24 also occurs considerably downfield from that of AH246, HM24, and HM246. We deduce that AH24 occurs as the doubly H-bonded system



with both nitro groups coplanar to the aromatic ring.

The observation of spin–spin coupling between NH and H_5 also is strong evidence that the amide (N_1) bond system is coplanar with the aromatic ring. Presumably, structures of Type (b) are important in accounting for the coupling. Consistent with this, we note that the *ortho* coupling between H_5 and H_6 is appreciably larger than the coupling between $H_{3,5}$ and H_6 in 2,6-dinitroanilines [Ref. 1, also Table II].

The downfield shift of the methyl peak of AH24 compared with the other acetamides is in concert[27] with increased double-bond character of the amide bond, as in Structure (c).

The location of H_3 in AH24 is the same as that in HM24 and HH24, and downfield from H_3 in AM24 and MM24. This may be ascribed to location of $(NO_2)_2$ coplanar with the ring in the former molecules. The upfield shift of the H_3 peak in AM24 is consistent with the (average) location of $(NO_2)_2$ out of the plane of the ring due to the steric effects of nonperpendicularity of the amide linkage and the ring, while the larger upfield shift of H_3 in MM24 betrays even greater cocking of $(NO_2)_2$ because of steric interference with the methyl groups. The downfield shift of H_6 in AM24, compared to HM24 and MM24 suggests that the cocking of the amide group leads to proximity of H_6 and the carbonyl oxygen atom.

Finally, HM24 shows a larger spin–spin coupling

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[31] L. A. LaPlanche, H. B. Thompson, and M. T. Rogers, J. Phys. Chem. **69**, 1482 (1965).

[32] The NMR evidence for the configurations and internal H bonding in various nitroanilines has been discussed in Ref. 1, as well as by I. D. Rae [Australian J. Chem. **18**, 1807 (1965); Chem. Comm. 519 (1966)], and by B. Lamm [Acta Chem. Scand. **19**, 1492, 2316 (1965)]. Relevant information has been obtained from optical spectroscopy also: For examples of recent work, see M. J. Kamlet, H. G. Adolph, and J. C. Hoffsommer [J. Am. Chem. Soc. **86**, 4018 (1964)] and L. K. Dyall and J. E. Kemp [Spectrochim. Acta **22**, 467 (1966), and references therein].

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between NH and H_5 than AM24 does, suggesting that here the double-bond character of C_1–N_1 is greater than in AH24, undoubtedly because there is no competing amide double-bond structure in the former. The NH position for HM24 is upfield from that of AH24, probably because N_1 is less positive in charge than in the latter due to decreased charge withdrawal, i.e., the over-all double-bond character of its bond.

ACKNOWLEDGMENTS

We would like to thank Dr. G. L. Goodman for many enlightening discussions and valuable assistance with interpreting our results. We are very grateful to members of Dr. J. J. Katz' group, particularly Miss G. Norman, for taking 100-Mc/sec NMR spectra and other assistance.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 46, NUMBER 8 15 APRIL 1967

Nonempirical Calculations of the Isotropic Hyperfine Splitting Constants of ^{13}C, ^{14}N, and ^{17}O in Simple Radicals

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(Received 23 November 1966)

The isotropic hyperfine splitting constants in ESR spectra for simple radicals $^{13}C^1H_3$, $^{14}N^1H_2$, and $^{17}O^1H$ have been calculated nonempirically by using a configuration-interaction method correct to the second order in the energy matrix elements. Included in the treatment are all the singly excited configurations plus certain types of doubly excited configurations. Each configuration is expressed in terms of the self-consistent-field molecular orbitals and virtual orbitals derived for the ground state. The molecular orbitals are expanded about a single center with an extended basis set of Slater-type orbitals.

The calculated hyperfine splitting constants for ^{13}C, ^{14}N, and ^{17}O are found to be 2.7, 0.9, and -0.5 G, respectively, when all the virtual orbitals with symmetry species A_1' or A_1 are used; the values are improved to 40.6, 19.0, and -35.4 G, respectively, when certain virtual orbitals with undesirable characteristics are excluded. Though not to be given serious consideration because of the nature of the wavefunctions employed, calculations for ^1H are carried out and the values are found to range from -4 to -7 G.

Attention is called to the possible danger in using virtual orbitals indiscriminately for calculations on ground-state properties other than energy. Based on the experience gained from this work we suggest that only the orbitals that are better approximations to the excited-state molecular orbitals be used.

I. INTRODUCTION

In the recent years the semiempirical theory for the isotropic hyperfine interactions in organic radicals and ions has made a most significant contribution to the application of ESR spectroscopy to organic chemistry.[1–3] Although the theory is well established and its validity beyond question, there is still room for refinement and further development. To accomplish this, information provided by detailed and nonempirical calculations both on the hyperfine splitting constants and charge distributions of the molecule would be needed. Unfortunately work along this line is sparse—the reason is mainly a lack of good molecular wavefunctions.

For the simple radicals and ions of the type AH_x, A being a second-row atom combined with x hydrogen atoms, computer programs have recently become available for the construction of self-consistent-field (SCF) wavefunctions for the ground states. The molecular orbitals (MO's) are expanded about a single center with an extended basis set of Slater-type orbitals (STO's).[4,5]

Obviously these one-center-expanded (OCE) molecular wavefunctions are ideal for nonempirical calculations for the simple reason that the dilemma of using approximations for the three- and four-center integrals no longer exists in this case. Further, these are relatively good molecular wavefunctions, shown by the fact that the energies given by these functions for the nine-electron systems deviate less than 0.5% and 1.3% from the estimated Hartree–Fock values and the experimental values, respectively.[5] It seems, there-

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[1] For example, see reviews on electron spin resonance given in Ann. Rev. Phys. Chem. beginning 1957. The papers cited in Refs. 2 and 3 are also helpful.

[2] H. M. McConnell and D. G. Chesnut, J. Chem. Phys. **28**, 107 (1958).

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