J. Am. Chem. Soc. 1983, 105, 4868-4870

in ortho-substituted acetanilide compounds.[23]

The predominant cis and nearly coplanar conformation found for AAF in solution resembled results previously reported for acetanilide in solution.[23] Though no attempt was made to estimate the average torsion angle about the aryl–nitrogen level of the cis form of AAF in solution, it may be thought of as being a compromise between the unfavorable steric interactions between the oxygen and the ortho protons and the resonance energy stabilization from $\pi$-electron delocalization from the nitrogen to the fluorene ring system. In the trans form, the average torsion angle for the aryl–nitrogen bond is predicted to be approximately 90° in solution, like that of N-substituted AAF compounds. Unfavorable steric interactions between the methyl group and the ortho protons apparently contribute to the destabilization and a coplanar conformation.

X-ray crystallography results have been reported for AAF[11] and N-HO-AAF,[12] each of which was in the cis form. The torsion angle between the planes of the fluorene ring and the acetamido moiety for AAF and N-HO-AAF was 42.2° and 16.6°, respectively. The reason for the apparent deviation from near coplanarity for AAF in the solid state is unclear. In solution, the upfield shifts of the carbons ortho and para to the acetamido moiety in the cis form of AAF and N-HO-AAF indicated that the averge torsion angle of the cis form of AAF was similar to and possibly less than that of N-HO-AAF.

## Conclusion

The conformation and dynamics about the aryl–nitrogen bond and the amide bond of AAF and several aryl amides with oxygen on the nitrogen atom have been investigated for the first time. An unusually favorable equilibrium distribution in N-HO-AAF and N-AcO-AAF enabled calculation of the barrier to rotation about the amide bond. The barrier for the amide bond was 14.4 ± 0.1 kcal/mol for N-HO-AAF and 13.7 ± 0.1 kcal/mol for N-AcO-AAF. Rotation about the aryl–nitrogen bond was rapid at the low temperatures that were utilized, but pronounced conformational preferences were observed. In the cis conformation about the amide bond, the acetamido moiety was approximately coplanar to the fluorene ring while in the trans conformation the acetamido and fluorene moieties were nearly orthogonal. This was manifested in large chemical shift differences between subspectra of the resonances from carbons ortho and para to the acetamido moiety and smaller differences in the second ring due mainly to delocalization of $\pi$-electron density from the nitrogen to both aromatic rings of fluorene. Resonances of the ortho protons could be shifted either upfield or downfield depending on the average torsion angle about the aryl–nitrogen band. The NMR data suggest a greater access to the conformational domains than is suggested from X-ray crystallography data. The results should be of value for interpretations concerning the orientation of the AAF moiety in modified oligonucleotides.

**Acknowledgment.** We acknowledge the NMR facility located at the University of South Carolina, which is supported by Grant No. CHE-78-18723 from the National Science Foundation for the $^{15}N$ NMR spectra. We also acknowledge the Quantum Chemistry Program Exchange at Indiana University for the Dynamic NMR program and Mr. Bruce A. Pearce at NCTR for adapting the program to the IBM 370 computer/Versatec plotter at NCTR.

**Registry No.** AAF, 53-96-3; N-HO-AAF, 53-95-2; N-AcO-AAF, 6098-44-8; N-$OSO_3H$-AAF, 16808-85-8.

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# On the Structure of Anions Derived from Cycloheptatriene in the Gas Phase

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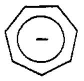
*Contribution from the Departments of Chemistry, University of California, Riverside, Riverside, California 92521, and the University of Nebraska—Lincoln, Lincoln, Nebraska 68588.*

*Received May 21, 1982*

**Abstract:** Fourier transform mass spectrometric studies of hydrogen–deuterium exchange in gas-phase anion–molecule reactions at $6 \times 10^{-6}$ torr have led to the conclusion that a species with the time-averaged symmetry of the cycloheptatrienyl anion (**2**) is formed by proton abstraction from cycloheptatriene (**1**) and then rapidly rearranges to the benzyl anion (**3**) when $OD^-$ (and possibly $ND_2^-$) is employed as the abstracting base. These conclusions are supported by the results for **1**-*7,7-d*$_2$ or **1**-*1,2,3,4*,5,6-*d*$_6$ and $OH^-$, which show the required scrambling of the label in **3**, and by results for $C_7H_7^-$ from toluene, which parallel those for $C_7H_7^-$ from **1** with $ND_3$ or $D_2O$ but not with $CD_3OD$. Anion **2** undergoes exchange but does not rearrange to benzyl in the presence of $CD_3OD$. Evidence was not obtained for electron autodetachment from **3** formed from **1**. Since such behavior is expected for unimolecular isomerization, it is concluded that rearrangement occurs predominantly in a complex between **2** and water.

Previously reported thermochemical,[3] hydrogen–deuterium (H–D) exchange,[4] and infrared multiphoton electron detachment[5] data have indicated that a stable cycloheptatrienyl anion (**2**) can be formed by deprotonation of cycloheptatriene (**1**) in the gas phase. Isomerization of **2** ($\Delta H_f° = 51.2 \pm 3$ kcal/mol)[3] to the more stable benzyl anion (**3**) ($\Delta H_f° = 23.8 \pm 3$ kcal/mol)[3] would be expected if the energy barrier(s) for this reaction were relatively small. However, this isomerization has not been observed either in the gas phase[3-5] or in solution.[6-8] We now report H–D exchange and isotopic labeling studies (by Fourier transform mass spectrometry (FTMS))[9] which demonstrate that this thermody-


**1**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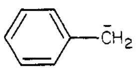

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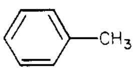

**4**

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[1] (a) University of California, Riverside. (b) University of Nebraska—Lincoln.

[2] Dedicated to Professor William v. E. Doering on the occasion of his 65th birthday.

[3] Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

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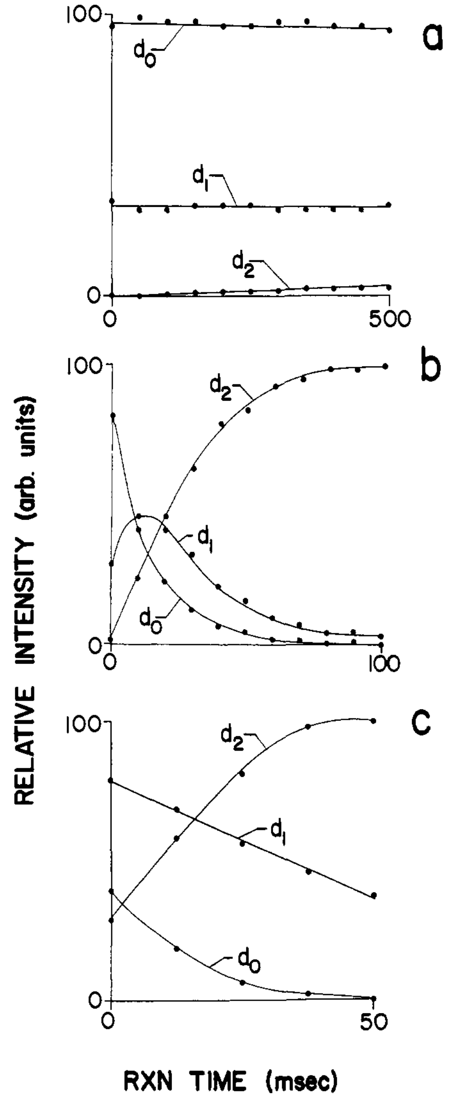

**Figure 1.** Hydrogen–deuterium exchange of $C_7H_7^-$ from toluene with (a) $ND_3$, (b) $D_2O$, and (c) $CD_3OD$. The time $t = 0$ is preceded by a 100-ms electron beam and a 10-ms ejection pulse for $ND_2^-$ or $OD^-$ in a and b, respectively, and by a 500-ms electron beam and a 10-ms ejection pulse for $CD_3O^-$ in c.

namically favored rearrangement can occur rapidly in the gas phase at low pressures ($<10^{-5}$ torr).

## Experimental Section

These studies were performed on a Nicolet FT/MS–1000 Fourier transform mass spectrometer equipped with a 3.0 T superconducting magnet and a 1 in. × 1 in. × 3 in. analyzer cell. The pressure of the toluene or cycloheptatriene was $3.5 \times 10^{-6}$ torr, whereas that of $ND_3$, $D_2O$, or $CD_3OD$ was $2.5 \times 10^{-6}$ torr, as measured with an uncalibrated ion gauge. The relative ion abundances in Figures 1 and 2 were measured *after* a 100-ms (500 ms in the case of $CD_3OD$) 7-eV electron pulse followed by a 10-ms ejection pulse on $ND_2^-$, $OD^-$, or $CD_3O^-$. Ion ejection pulses can be used to eject selected ions from the analyzer cell either during ion formation or anytime during the reaction period which follows. This technique can be used either to select a given ion and follow its reactions by ejecting all other ions or to link a reactant ion to a possible product by ejecting the reactant and observing the effect on product ion signal (conventional double resonance experiment). Both modes were employed in this study.

Cycloheptatriene-*7,7*-$d_2$ (**1**-$d_2$) (7.4% $d_0$, 16.5% $d_1$, and 76.1% $d_2$ by mass spectrometry) and cycloheptatriene-*1,2,3,4,5,6*-$d_6$ (**1**-$d_6$) (95.0% $d_6$ and 4.5% $d_5$ by mass spectrometry, and >98% deuteration at $C_1$–$C_6$ by NMR spectrometry) were prepared by the cuprous chloride catalyzed decomposition of diazomethane-$d_2$ or diazomethane in the presence of benzene[10,11] or benzene-$d_6$,[6,11] respectively. All samples of **1**, **1**-$d_2$, and **1**-$d_6$ were purified by gas chromatography on a 1-m 25% Carbowax 1540 on 100/120 mesh Chromosorb P column at 50 °C.

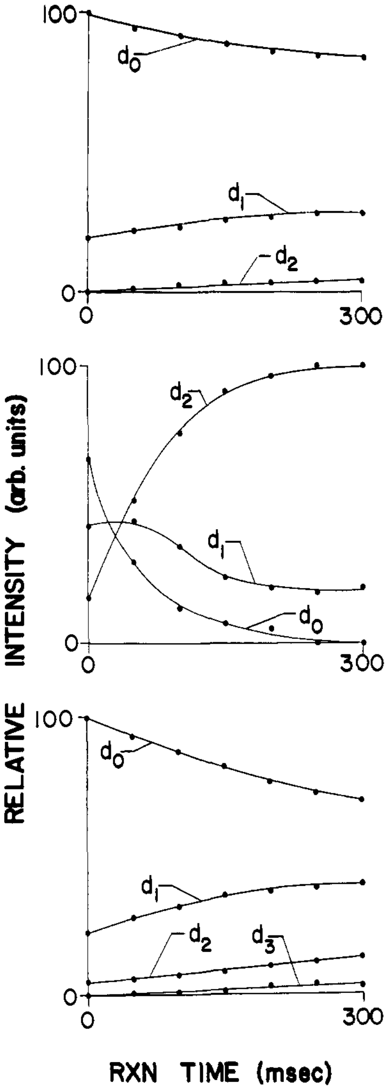

**Figure 2.** Hydrogen–deuterium exchange of $C_7H_7^-$ from cycloheptatriene with (a) $ND_3$, (b) $D_2O$, and (c) $CD_3OD$. The time $t = 0$ is preceded by the events stated in the caption to Figure 1.

## Results and Discussion

The $C_7$ anions from toluene (**4**) and cycloheptatriene (**1**) were generated by proton abstraction with $ND_2^-$, $OD^-$, or $CD_3O^-$ which were themselves readily produced by a low-energy (ca. 7 eV) electron bombardment of $ND_3$, $D_2O$, or $CD_3OD$, respectively. The $ND_2^-$, $OD^-$, or $CD_3O^-$ ions were then ejected from the cell and the ion intensities plotted as a function of time in the presence of a deuterated exchange reagent (Figures 1 and 2). Double resonance experiments showed in each case that exchange occurred between the $C_7$ anion and the *neutral* exchange reagent and that when multiple exchanges were observed they were sequential.

As seen in Figures 1b and 1c, reaction of $C_7H_7^-$ from toluene with $D_2O$ or $CD_3OD$ rapidly produced two and only two H–D exchanges,[11] in accord with formation of the benzyl anion. Furthermore, exchange between **3**-$d_2$ (from toluene-$\alpha,\alpha,\alpha$-$d_3$) and $H_2O$ showed two H–D exchanges with data closely parallel to that in Figure 1b, thereby confirming that the benzylic hydrogens were indeed the ones undergoing exchange.

The cycloheptatriene data in Figure 2c do not parallel those in Figure 1c. First, three H–D exchanges of almost equal rates

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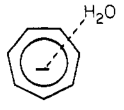
are observed in contrast to the two rapid exchanges observed in the latter figure, in accord with formation of the cycloheptatriene anion (**2**) from **1**. Furthermore, $CD_3O^-$ was regenerated (after being initially ejected from the FTMS cell) from $C_7H_7^-$ derived from toluene *but not from cycloheptatriene*. Deuteron abstraction from $CD_3OD$ is expected from the benzyl anion but not from the cycloheptatrienyl anion on the basis of the relative acidities of methanol, **1**, and **4** ($\Delta H^\circ_{\text{acid}}(CH_3OH) = 379.2 \pm 2$ kcal/mol; $\Delta H^\circ_{\text{acid}}(\mathbf{1}) = 373.9 \pm 2$ kcal/mol; $\Delta H^\circ_{\text{acid}}(\mathbf{4}) = 379.0 \pm 2$ kcal/mol).[3]

In contrast with Figure 2c, exchange of $C_7H_7^-$ from cycloheptatriene with $D_2O$ (Figure 2b) occurs rapidly to produce a twice-deuterated $C_7$ anion. In fact, the data in Figure 2b are almost identical with those in Figure 1b. This provides strong evidence that the species generated from cycloheptatriene and $OD^-$ and subsequently undergoing H–D exchange with $D_2O$ *is the benzyl anion* (3).

The foregoing results establish that the benzyl anion is ultimately formed from cycloheptatriene and $OD^-$ under FTMS conditions, but they do not establish that the cycloheptatrienyl anion is an intermediate. This latter point was investigated by monitoring the H–D exchange of $C_7$ anions formed from **1**-$d_2$ and **1**-$d_6$ with $H_2O$. Only one and two H–D exchanges, respectively, occurred for these compounds to afford *equilibrium* ratios of $d_1/d_0 = 2.2 \pm 0.4$ for **1**-$d_2$ and $d_4/d_5 = 2.6 \pm 0.4$ for **1**-$d_6$. If all seven positions become equivalent, then rearrangement of **1**-$d_2$ will afford **3** with $^5/_7$ of the deuterium atoms on the phenyl ring and $^2/_7$ at the benzylic position. Hence $d_1/d_0$ and $d_4/d_5$ values of 2.5 would ultimately be expected on exchange of the anions from **1**-$d_2$ and **1**-$d_6$, respectively, with $H_2O$. Thus, these results are completely consistent with deprotonation of **1** to form a cycloheptatrienyl anion–water complex which either possesses or affords one (or more) species which possess the time-averaged symmetry of **2**.

Rearrangement of **1** to **3** appears to be dependent on the basicity of the reagent ion ($OD^-$ or $CD_3O^-$). This can be rationalized by assuming that the energy barrier for rearrangement cannot be surmounted with the energy released by complex formation and proton abstraction in the case of the weaker base ($CD_3O^-$) but can be traversed in the case of $OD^-$ ($\Delta H^\circ_{\text{acid}}(H_2O) = 390.8 \pm 0.4$ kcal/mol).[3] Note that if this is the case, then benzyl anion formation would also be expected in the case of $ND_2^-$. This prediction is supported by the very close parallel between Figures 1a and 2a. However, this result is inconclusive due to the low level of H–D exchange which results from the large acidity difference between ammonia ($\Delta H^\circ_{\text{acid}}(NH_3) = 403.6 \pm 1$ kcal/mol[3]) and **1** or **4**.[12]

Finally, we wish to make several observations concerning the mechanism of this novel rearrangement. First, we believe it to be predominantly a bimolecular mechanism (i.e., we speculate that proton abstraction, rearrangement, and exchange may well occur within the collision complex (**5**)) since unimolecular isomerization of **2** could well result in autodetachment[14] of an electron from **3** due to the fact that **2** is less stable ($\Delta H_f{}^\circ{}_{298}(\mathbf{2}) = 51.2 \pm 3$ kcal/mol)[3] than a benzyl radical ($\Delta H_f{}^\circ{}_{298} = 44.2 \pm 4.5$ kcal/mol)[3] plus an electron. In a bimolecular process excess energy could be transfer to the departing HOD molecule and thus stabilize the benzyl anion which is formed. However, the occurrence of *some* electron autodetachment cannot be ruled out on the basis of our data. It is interesting to note that **3** is not formed on deprotonation of **1** by $OH^-$ in a flowing afterglow, presumably because the initially formed **2** can be rapidly cooled by collisions at the relatively high pressures (0.5 torr) of the experiment. Finally, a cycloheptatriene–norcaradiene isomerization[16] followed by bridgehead deprotonation and electrocyclic opening of a cyclopropyl anion[17,18] represents one possible pathway for this reaction.



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**Registry No. 1**, 544-25-2; **1**-*7,7*-$d_2$, 3101-97-1; **1**-*1,2,3,4,5,6*-$d_6$, 57412-92-7; **2**, 29875-65-8; H, 1333-74-0; $HO^-$, 14280-30-9; $H_2N^-$, 17655-31-1; MeOH, 67-56-1; $H_2O$, 7732-18-5.

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(12) The $d_1$ (and $d_2$) ions at "$t = 0$" in Figures 1c and 2c were formed during the 500-ms ionization and 10-ms ejection pulses. In contrast, the $d_1$ ions at "$t = 0$" in Figures 1a and 2a were possibly formed by multiple proton transfers within the initial ion–molecular complex.[13] The corresponding values in Figures 1b and 2b can be considered to arise from a combination of the above two effects.

(13) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.*, in press.

(14) We thank Professor J. L. Beauchamp for comments concerning this point. Note, however, that Brauman has recently reported interesting results suggesting that electron autodetachment does not always occur, even when it is energetically favorable.[15]

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