Carbon-13 Nuclear Magnetic Resonance Spectroscopy, a Probe to Dynamic Solvation. Anisotropic and Internal Motion in Aminobiphenyls and Their Salts

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Abstract: Carbon-13 spin-lattice relaxation times (T_1's) of the compounds 3- and 4-aminobiphenyl in a number of solvent systems and of the corresponding ammonium ions in acidic and nonacidic media indicate that molecular tumbling is anisotropic for these species. In addition, the known biphenyl geometry allows identification and semiquantitative evaluation of internal rotation–libration motions. The molecular dynamics of the amines and ammonium ions are qualitatively different. The protonated amine function is motionally more restricted by solvent-solute and ion-pair interactions. Thus in the 3-biphenylammonium ion, the principal axis for molecular reorientation is aligned close to the C_3- - -NH_3 bond axis ($\theta = 37°$, where θ is the angle between the biphenyl C_2 symmetry axis and the principal axis), whereas in the amine the principal axis lies closer to the biphenyl symmetry axis ($\theta = 12°$). In both the 3- and 4-aminobiphenyl systems the unsubstituted phenyl ring is more mobile due to rapid, phenyl group rotation or libration. The result of this internal motion is particularly marked for the 3-aminobiphenyl systems and for protonated 4-aminobiphenyl in acetic acid where the 2′ and 3′ T_1's are 40–60% longer than expected based on a rigid nonplanar biphenyl model. Variable temperature T_1 studies give activation energies for overall molecular reorientation (rotational diffusion): 4-biphenylammonium ion in acetic acid ca. 12 kcal/mol; 4-biphenylammonium ion in trifluoroacetic acid 8 kcal/mol; biphenylammonium salt and the amine in two neutral organic solvents about 4 kcal/mol.

The importance of ^{13}C spin-lattice relaxation (T_1) measurements as a tool for obtaining information about microdynamic behavior in liquids[2] and their use to assign resonances in ^{13}C NMR spectra[3] have been well documented. Spin-lattice relaxation of ^{13}C nuclei in typical organic compounds is largely dominated by dipole-dipole interactions with nearby protons, T_1^{DD} being inversely proportional to the number of directly attached protons for CH, CH_2, and CH_3 carbons in molecules that are rigid and that reorient *isotropically.* In this case for a given carbon, T_1 is also an inverse monotonic function of molecular tumbling. Interpretation of T_1 data in medium-sized molecules reorienting anisotropically or with internal flexibility may be complicated even when ^{13}C–^1H dipole-dipole interactions dominate the ^{13}C relaxation behavior.[2,4] In some *symmetric* and *asymmetric* top molecules quantitative information can be obtained about rotational diffusion around the different axes using calculations derived from the work of Woessner[5a] or Huntress.[5b]

Semiquantitative calculations of the anisotropic motion of monosubstituted benzenes have shown that the rotation around the C_2 symmetry axis is favored to a varying degree over the motion about the other axis lying in the plane of the benzene ring.[2c] (Motion around the axis perpendicular to the ring cannot be probed directly by this NMR method since the effective correlation time, τ_{eff}, is a function of three reorientation times for rotation about axes x, y, z but only two independent T_1's are available, both functions of C–H vectors lying in the plane of the benzene ring.)[6] In the case of aniline this preference is observed only in acidic solvents where the amine group is protonated.[2c]

In this paper we have looked at the relaxation behavior of 4-aminobiphenyl (I) and 3-aminobiphenyl (II) in various solvent systems. In these compounds in addition to the anisotropic overall motion an internal motion has to be considered. Indeed, we want to report that accurate[7] spin-lattice relaxation data obtained at 67.9 MHz indicate different T_1 values for the two rings in both I and II.

Results and Discussion

Carbon-13 Chemical Shifts. The assignment of the ^{13}C resonances for I (see Figure 1) was achieved by comparison with the corresponding solvent shifts for aniline[2c] and by using the literature assignment for I in acetone solution;[8] the T_1 pattern discussed below allowed a check for these assignments. The pronounced high-field shift, going from the amine to the ammonium ion, for C-4 (and to a lesser extent for C-1′) and the low-field shifts for C-3 and C-1 are expected from charge density considerations.[9]

The signals for the carbons ortho to the NH_3^+ group and that for the carbon substituted by the NH_3^+ group are somewhat broader in solutions of IA in DMF and IB in $MeCO_2H$. The same is true for 3-biphenylammonium trifluoroacetate in MeCN.

Broadening of the signal for a carbon substituted by NH_3^+ group, has been attributed to unresolved scalar coupling with cationic nitrogen.[10] For the ortho and para carbons the broadening indicates that rapid chemical exchange (protonation, deprotonation) occurs. The example of IA in DMF where the chemical shifts are dependent upon temperature, is illustrative (see Table I). Chemical exchange will affect the line widths of carbons that undergo large changes in shielding on protonation. (However, the exchange process will not directly affect T_1, since the equilibrium constant for the deprotonation of the ammonium ion is very small, e.g., $\sim 10^{-6}$ for anilinium ion in ethanol.)[11]

Upfield shifts for C-4 and downfield shifts for C-1 and C-3 are observed when one compares solutions of IA in MeOH with MeOH solutions of IA containing added trifluoroacetic acid (TFA) (Table I). These shifts may be caused by the change in the nature of ion pairs, formation of larger ion complexes.

The assignment of resonances in the 3-aminobiphenyl system was achieved by comparison with the shifts of aniline and its salts and also with the spectrum of biphenyl.[8] Again, the observed T_1 pattern provides a check on the assignments. In all solutions except TFA the highest field resonance belongs to C-2. For the TFA solution, the T_1 for the high-field signal is half that of the nearest downfield resonance and therefore the spectral assignment for C-4 and C-2 is reversed[2a] for the TFA solution (see Table I). Upon protonation, chemical shift changes are generally analogous to those observed for the para series.

^{13}C T_1 Data. 4-Aminobiphenyl and Its Cation. The T_1

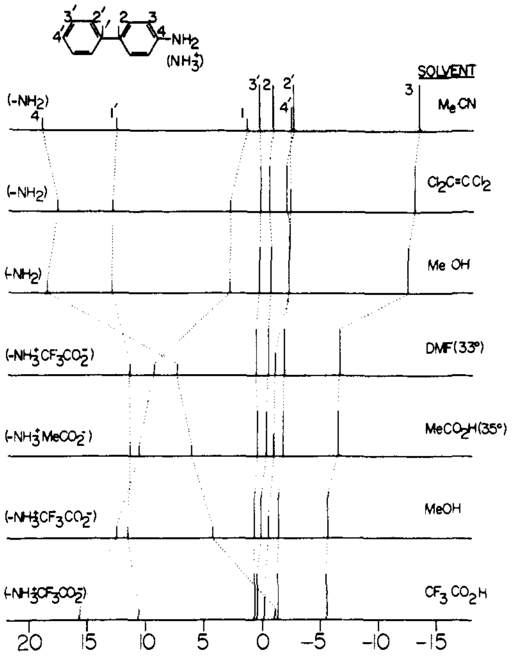

Figure 1. Chemical shifts (in ppm) for 4-aminobiphenyls relative to internal benzene.

data for the C-H carbons shown in Table II have some similarities with the T_1 values for aniline; the anisotropy of molecular tumbling increases significantly when the amino group is protonated (Table II). By comparing the ratios $T_1(2,3)/T_1(4')$ for I with the analogous ratios ($T_1(2,3)/T_1(4)$) for aniline one should give attention to the fact that the parent compound, biphenyl, already undergoes preferential rotation around the C_2 molecular axis (T_1 ratio = 1.8).[2c] For I the overall motion is relatively fast for the amine in all solvents and for the ammonium trifluoroacetate in the polar solvent methanol; overall motion is slower (T_1's are shorter) for the ammonium ion in acetic and trifluoroacetic acids. It is worthwhile to note that in the case of nonprotonated amine, the change of solvent from aprotic (MeCN) to protic (MeOH) slows the overall motion, due presumably to hydrogen bonding interactions.[11b]

Table II gives the ratios for $T_1(2',3')/T_1(2,3)$. Molecular symmetry considerations require that the origin of different T_1 values for the two rings cannot be simply explained by overall anisotropic rotational motions. Instead, the differences must be accounted for by an *internal motion.* The ratios $T_1(2',3')/T_1(2,3)$ can be explained by assuming that the internal motion for the amino-substituted ring (ring A) is more restricted by solvent-solute interactions.

Two kinds of internal motion should be considered: (1) internal phenyl *group rotation* around the Cl-Cl′ bond and (2) *torsional vibration* (*libration*), since full rotation around the Cl-Cl′ bond on an appropriate time scale might be excluded because of a high barrier for that rotation. There is considerable theoretical evidence that the barrier of rotation is 2-5 kcal/mol while passing the 90° twisting angle ($\phi = 90°$)[12] and within the range 0.5-3 kcal/mol for the $\phi = 0°$ angle.[12c,13] It should be mentioned that experimental estimates showed that biphenyl in solution has neither a planar structure nor free rotation but exists in a twisted conformation ($\phi = 45 \pm 15°$).[14] Two recent estimates, from indirect studies, indicate ϕ may be close to 30°.[15,16] One of these papers[15] cites earlier references which are largely contradictory to themselves and the later work.

The quantitative contributions of hindered full phenyl rotation and internal librational motion are not known at present. We feel that the librational motion is at least partially effective in the aminobiphenyl system. A librational mode operating within the two favorable equilibrium ring-ring dihedral angles for the biphenyl molecule (i.e., ca. 30° angle between the phenyl rings) would be energetically possible. A librational amplitude as high as 180° − (2)(30°) = 120° might thus be anticipated.

Comparing T_1 values for the carbons C-2 and C-3 with C-2′ and C-3′, a variation with solvent is revealed. While there is a maximal T_1 differential in acetic acid ($T_1(2',3')/T_1(2,3) = 1.45$) there is a minimal observed difference in trifluoroacetic acid (ratio: 1.02). Although the overall motional rate is similarly slow in acetic acid and trifluoroacetic acid, it is surprising that the B/A ring T_1 ratio is most different in these two solvent systems. This may be a result of restriction of internal motion of the substituted ring (A) in acetic acid due to strong interaction with the acetic acid solvent sphere, counterions, etc., around the protonated amino group. A strong interaction such as proposed is consistent with the fact that I reacts with acetic acid over a longer time scale. Variable temperature studies for these compounds were hampered because of stability (higher temperature) and solubility problems (see also the Experimental Section). Nevertheless reasonably reliable values for the energy of activation, E_a ($1/T_1 = 1/T_1^0 \exp(E_a/RT)$), for molecular tumbling may be obtained.[7] Interestingly the slope of the plot for $\ln T_1$ vs. $°K^{-1}$ is the same for all carbons in the compounds at hand.

As a partial check for our temperature measurements T_1's were obtained for 4-methylbiphenyl over the same range of temperatures. The value of 4 kcal/mol for the activation energy for the 4-methylbiphenyl (see below) is in a very good agreement with the accurate temperature study (over the range 278-378 K) of the similar system, 3-bromobiphenyl, for which E_a = 5 kcal/mol was found,[17] somewhat higher than the activation energy of tumbling for 4-methylbiphenyl.

Activation energy, kcal/mol

IB in $MeCO_2H$	IA in CF_3CO_2H	IA in MeOH	I in CCl_4	$Me-C_6H_4-C_6H_5$
12 ± 2	8 ± 2	~4	~4	4 ± 1

For the aminobiphenyl-acetic acid system, the apparent activation energy is the highest value reported to our knowledge. This may be a result of particularly strong solvation or complexation effects for the ammonium ion in acetic acid (vide supra). For the solutions IA in MeOH, I in CCl_4, and 4-methylbiphenyl in acetone-d_6 E_a is ca. 4 kcal/mol while the $T_1(2,3)/T_1(4')$ ratios are 3.7, 1.8, and 1.8, respectively. Thus, a smaller activation energy does not necessarily require an increase in the anisotropy of motion, as suggested by Imanari et al.[18] The high activation energy for IB in acetic acid is also consistent with a "complexation" with the solvent system as noted in the previous section.

^{13}C T_1 Data. The 3-Aminobiphenyl System. In the 3-aminobiphenyl system, II, the situation is more complex since there is no longer a simple C_2 molecular symmetry axis. Interpretation of the T_1 ratios for both rings in II requires consideration of several effects including differential internal motion of the A and B rings around the biphenyl axis and the effect on T_1's of noncoplanarity of the two rings relative to a principal molecular diffusion axis that is not coincident with the biphenyl axis. In order to assess the contribution of these two factors semiquantitative calculations were carried out on the representative systems: II in $Cl_2C{=}CCl_2$ (the lowest $T_1(4)/T_1(6)$ ratio), IIA in MeOH

Table I. Carbon-13 Chemical Shifts[a] for 4-Methylbiphenyl, 4-Biphenylammonium Trifluoroacetate (IA), 3-Aminobiphenyl (II), 3-Biphenylammonium Trifluoroacetate (IIA), and Chloride (IIB)

			Carbon atom									
Compd	Solvent	Concn[b]	1′	2′	3′	4′	1	2	3	4	5	6
4-Methyl-biphenyl	Acetone-d_6	2	12.69	−1.54	0.50	−1.32	9.87	−1.60	1.25	8.56	1.25	−1.60
IA	DMF	2[c]	11.51	−1.75	0.65	−0.95	9.46	−0.41	−6.65	7.71	−6.65	−0.41
		2[d]	11.74	−1.78	0.62	−1.08	8.85	−0.43	−7.12	8.54	−7.12	−0.43
IA	MeOH	1	11.51	−1.37	0.68	−0.48	12.82	0.15	−5.45	3.82	−5.45	0.15
IA	MeOH, CF_3CO_2H (19:1 v/v)	0.9	11.34	−1.33	0.68	−0.33	13.81	0.19	−4.81	2.32	−4.81	0.19
IA	MeOH, CF_3CO_2H (4:1 v/v)	0.8	11.36	−1.33	0.67	−0.29	13.97	0.21	−4.75	2.17	−4.75	0.21
II	$Cl_2C{=}CCl_2$	2	13.34	−1.19	0.27	−1.26	14.00	−14.54	19.73	−14.26	1.26	−10.97
II	MeOH	2	13.47	−1.35	0.36	−1.19	14.08	−14.17	19.60	−13.68	1.28	−11.11
IIB	MeOH	2	11.28	−1.37	0.70	−0.17	14.68	−7.03	4.19	−6.75	2.15	−1.46
IIB	MeOH $MeCO_2H$(3:1 v/v)	2	11.08	−1.29	0.79	−0.08	14.88	−6.70	3.82	−6.90	2.20	−1.18
IIA	MeCN	0.95[e]	11.31	−1.44	0.68	−0.34	14.27	−8.49	6.96	−8.09	1.89	−3.47
		0.95[c]	11.18	−1.46	0.68	−0.31	14.22	−8.20	6.33	−7.80	1.91	−3.09
IIA	MeOH	1.4	11.48	−1.29	0.73	−0.20	15.12	−7.74	5.95	−7.52	2.14	−2.29
IIA	CF_3CO_2H	2	10.44	−1.46	0.69	0.17	16.17	−7.26	0.69	−7.37	2.42	0.60

[a] Parts per million relative to internal benzene standard, positive shifts downfield (based on TMS convention). [b] Concentration in moles per 1000 ml of solvent, [c] Temperature 33°. [d] Temperature 45°. [e] Temperature 40°.

Table II. Carbon-13 T_1 Data for 4-Aminobiphenyl (I), 4-Biphenylammonium Trifluoroacetate (IA), Acetate (IB), and 4-Methylbiphenyl

				T_1, sec						
Compd	Solvent	Concn[a]	Temp, °C	4′	3′	2′	2	3	$T_1(2,3)/T_1(4')$	$T_1(2',3')/T_1(2,3)$[b]
4-Methyl-biphenyl	Me_2CO-d_6	2	45	4.0	7.22	7.30	7.30	7.22	1.81	1.00
			41	3.9	6.40	6.20	6.20	6.38	1.62	1.00
			35	3.1	5.88	5.89	5.96	5.80	1.89	1.00
I	MeCN	2	39	2.63	4.80	4.89	4.38	4.42	1.67	1.10
I	$Cl_2C{=}CCl_2$	2	36	1.59	3.32	3.38	2.85	2.90	1.84	1.15
I	CCl_4	2	42	1.41	3.21	3.29	2.78	2.85	1.90	1.15
			35	1.37	2.85	3.04	2.51	2.50	1.83	1.18
I	MeOH	2	39		4.03		3.27	3.25		1.24
IB	$MeCO_2H$	2.3	45	0.59	1.96	2.08	1.41	1.39	2.37	1.44
			35	0.29	1.08	1.11	0.77	0.74	2.58	1.45
			29	0.22	0.75	0.76	0.52	0.53	2.39	1.44
IA	DMF	2	38	0.45	1.42	1.44	1.24	1.22	2.73	1.16
IA	MeOH	1	39	0.81	3.31	3.36	3.10	2.90	3.70	1.11
			33	0.75	2.86	3.02	2.60	2.52	3.41	1.15
IA	MeOH CF_3CO_2H (19:1 v/v)	0.9	33	0.60	2.35	2.32	2.03	1.96	3.30	1.17
IA	MeOH CF_3CO_2H (4:1 v/v)	0.8	39	0.77	2.92	3.13	2.63	2.68	3.45	1.14
IA	CF_3CO_2H	2.4	45	0.39		1.33		1.30	3.31	1.02
			39	0.30		1.09		1.00	3.33	1.09
			29	0.19	0.62	0.64	0.61	0.61	3.25	1.03

[a] Concentration in moles per 1000 ml of solvent. [b] Ring B/ring A T_1 ratio.

(high $T_1(2,5)/T_1(6)$ and $T_1(2,5)/T_1(4)$ ratios), and IIA in MeCN (the highest $T_1(4)/T_1(6)$ ratio) (see Table III).

The molecules were first assumed to be rigid. T_1's were computed for carbons 2′ and 3′, as functions of the twisting angle, ϕ, between the two phenyl planes.

The "rigid" biphenyl molecules were treated as symmetric ellipsoids.[19] This approximation may be justified on the basis of the following reasoning. The reorientation time around the preferred axis of rotation ($\tau_z \equiv \tau_\parallel$) is expected to be substantially shorter than the reorientation time around either perpendicular axis (τ_x, τ_y are approximated here to be equal $\tau_x \simeq \tau_y \simeq \tau_\perp$; $\tau_\perp/\tau_\parallel \equiv \rho > 1.0$). The "ellipticities" E_x and E_y, as defined by Grant,[4a] will be more similar to each other in the nonplanar biphenyl molecule than for the planar case (for the twisting angle ϕ = 90°, $E_x = E_y$). Moreover, the polar amino functions "disturb solvent" equally during reorientation around these two perpendicular axes.

The relaxation times for a symmetric top molecule (an approximation used here) follow:[20,5a]

$$1/T_1{}^i = (\text{constant})\tau_\parallel \chi_i(\theta_i,\rho)$$

where $\chi_i(\theta_i,\rho)$ is the function of ρ defined above and θ_i is the angle between the C–H vectors and the preferred axis of rotation. In our case we need to independently determine only one angle, θ_4, the angle for the C4–H vector. The other angles can be readily obtained from the known biphenyl geometry. The three relaxation times $T_1(4)$, $T_1(6)$, $T_1(2)$ fix the direction of the principal axis and determine the spinning ratio, ρ. Results for the amine and ammonium ion in acetonitrile are shown in Figure 3.

Table III. Carbon-13 T_1 Data for 3-Aminobiphenyl (II), 3-Biphenylammonium Trifluoroacetate (IIA), and Chloride (IIB)

Compd	Solvent	Concn[a]	Temp, °C	T_1, sec 4′	3′	2′	3	4	5	6	$T_1(4)/T_1(6)$	$T_1(2,5)/T_1(6)$	$T_1(2,5)/T_1(4)$	$T_1(2',3')/T_1(4')$	$T_1(2',3')/T_1(x)$[b]
II	$Cl_2C{=}CCl_2$	2	38	1.4	2.73	2.6	2.16	1.32	1.95	1.78	0.74	1.15	1.56	1.90	1.43
II	MeOH	2	45	2.17	4.35	4.30	3.30	2.20	3.55	2.87	0.77	1.19	1.56	1.99	1.39
IIB	MeOH	2	45	1.42	2.60	2.72	1.87	1.37	1.78	1.09	1.26	1.67	1.33	1.87	1.95
IIB	MeOH $MeCO_2H$(3:1 v/v)	2	45	1.02	2.13	2.13	1.35	0.96	1.23	0.93	1.03	1.39	1.34	2.09	1.97
IIA	CF_3CO_2H	2	31	0.35	0.91	0.85	0.58	0.34	0.46	0.34	1.06	1.50	1.50	2.37	2.15
IIA	MeOH	1.4	39	1.32	2.94	2.96	1.81	1.26	1.82	1.00	1.26	1.82	1.44	2.24	2.29
IIA	Me_2CO $MeCO_2Et$(1:2 v/v)	2	35	1.01	2.04	2.06	1.28	0.92	1.26	0.70	1.31	1.82	1.40	2.03	2.27
IIA	MeCN	0.95	33	1.97	3.33	3.37	2.29	1.80	2.24	1.32	1.36	1.72	1.26	1.70	2.00

[a] Concentration in moles per 1000 ml of solvent. [b] $T_1(x) = 0.5/T_1(2,5) + 0.5/T_1(6)$.

Table IV.

		Dihedral angle ϕ =				
	Exptl	0°	30°	45°	70°	90°
$T_1(2',3')$[a]	2.70	1.91	1.92	1.95	1.92	1.94
$T_1(2',3')$[b]	2.95	1.29	1.36	1.46	1.69	1.80
$T_1(2',3')$[c]	3.35	1.67	1.82	1.93	2.15	2.20

[a] II in $Cl_2C{=}CCl_2$. [b] IIA in MeOH. [c] IIA in MeCN.

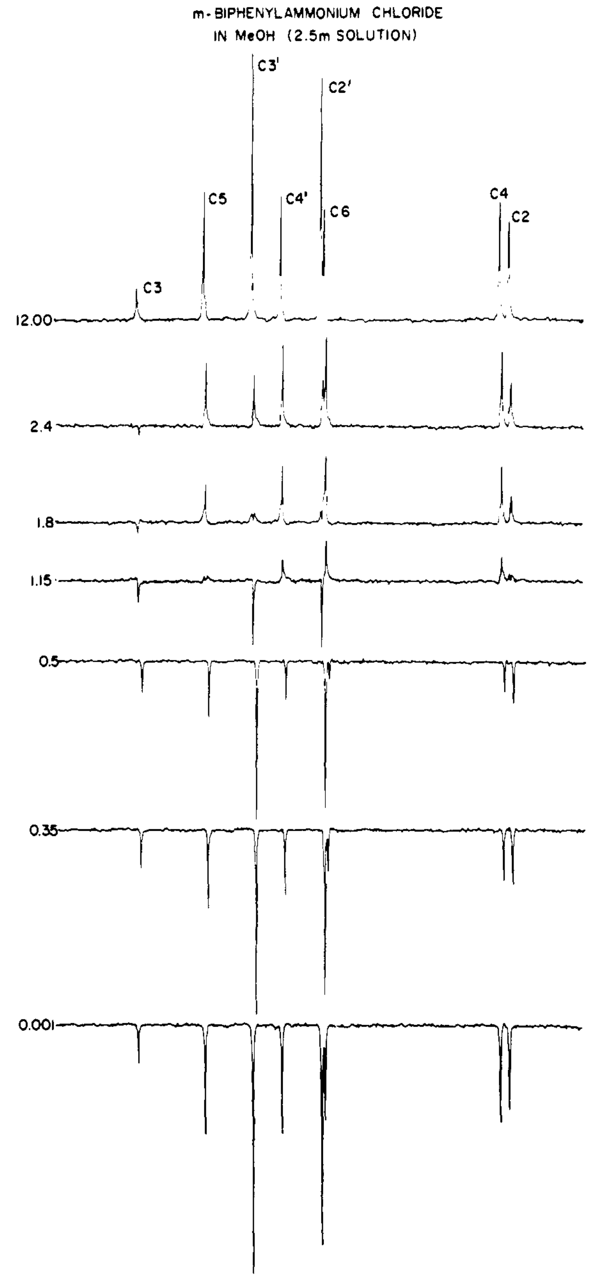

Figure 2. Set of IRFT spectra using the unmodified inversion-recovery sequence. Number to the left of each spectrum is the τ value in seconds (70 scans, 1000 Hz spectral width).

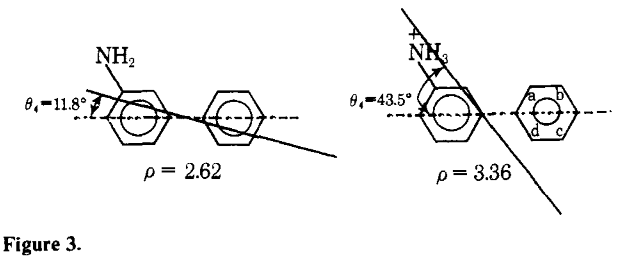

Figure 3.

For comparison, calculations indicate that for IIA in methanol $\theta_4 = 36.7°$ and $\rho = 4.83$.

The relaxation times of the carbon atoms 2′ and 3′ are equally weighted averages of the relaxation times $T_1(\mathrm{a})$ and $T_1(\mathrm{d})$ (see diagram above): $1/T_1(2',3') = 0.5/T_1(\mathrm{a}) + 0.5/T_1(\mathrm{d})$. $T_1(\mathrm{a})$ may be easily calculated because it differs from that of $T_1(6)$ only through the difference in θ_i angles, i.e., $T_1(\mathrm{a}) = \chi(\theta_6,\rho)/\chi(\theta_\mathrm{a},\rho)T_1(6)$. The same is true for the pair $T_1(\mathrm{d})$ and $T_1(5)$. If the molecule is planar then $T_1(\mathrm{d})$ will be equal to $T_1(5)$ and $T_1(\mathrm{a})$ will be equal to $T_1(6)$. $T_1(\mathrm{a})$ and $T_1(\mathrm{d})$ become functions of the dihedral angle, ϕ, between the two phenyl rings since θ_a and θ_d then vary. The calculated $T_1(2',3')$ for the different dihedral angles ϕ are presented in Table IV.

Several conclusions may be drawn. For the amine case the modulation of T_1 due to noncoplanarity of the molecule is, as expected, small. The ratios of T_1's ($\simeq 1.4$), given in the last column of Table III, monitor the internal motion between the two phenyl rings. For the ammonium salts, this modulation is greater. The differentiation in T_1's due to internal motion should be greater or similar to the amine case. In the ammonium ion $T_1(2',3'\text{ observed})/T_1(2',3'\text{ rigid})$ should be approximately 1.7–1.8. This indicates that libration occurs around the averaged twisting angle, ϕ, 30 to 50° for aminobiphenyls in *solution* (Table IV). Even for $\phi = 90°$, $T_1(2',3'\text{ observed})/T_1(2',3'\text{ rigid})$ is equal to ~ 1.5.

For the 3-aminobiphenyl system internal motion thus affects the T_1 behavior more strongly. Whether the internal motion is faster in the 3-aminophenyl case is not certain. The reason for this lies not only in the approximation used here but mainly in the complex relationship between the correlation times for internal motions (proceeding at various angles with respect to the principle axis) and for overall *anisotropic* motion.

Experimental Section

4-Aminobiphenyl was obtained from Aldrich Chemical Co. The compound was recrystallized from an alcohol-water mixture before using. 3-Aminobiphenyl was synthesized by the reduction of 3-nitrobiphenyl according to Blakey et al.[20] The trifluoroacetate salts were prepared by adding the appropriate amounts of trifluoroacetic acid into ether solutions of the aminobiphenyls, washing with ether, and drying overnight under vacuum. Slow decomposition occurs when aminobiphenyls are kept in solution significantly above room temperature. Also, after several hours in acetic acid at ca. 55°, 4-aminobiphenyl reacts to form 4-phenyl(acetanilide).

Spin-lattice relaxation times were obtained with complete decoupling on a Bruker HX-270 (67.9 MHz) using the IRFT pulse sequence. Spectral widths of 1500–4000 Hz were used ($\pi/2$ pulse $\equiv 16\ \mu$sec) with acquisition of 8K data points. Figure 2 gives a set of ^{13}C IRFT spectra for a typical run. Reported T_1's are averages for two runs. Sets of 11–13 τ values were used for the T_1 determination. The accuracies of T_1 measurements in this study range from ±5 to ±10% depending on the solution concentration and the signal-to-noise ratio (T_1's are reported to 0.01 sec in the tables even when accuracy limitations are $\gtrsim\pm 0.1$ sec).

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