Proton Magnetic Resonance Studies of Rotational Isomerism in Halotoluenes. X. Estimates of Conformational Preferences and Rotational Barriers in Benzal Fluoride and Some Dichloro Derivatives

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The synthesis of benzal fluoride and of its 2,6-, 3,5-, 3,4-, and 2,4-dichloro derivatives is followed by an analysis of their proton magnetic resonance spectra. The long-range spin-spin coupling constants are most consistent with a barrier to rotation about the sp^2-sp^3 carbon-carbon bond in benzal fluoride of less than 500 cal/mol, in semiquantitative agreement with an *ab initio* molecular orbital calculation. The 2,6-dichloro derivative has a conformation in which the C—H bond of the side chain lies in the plane of the aromatic ring. The 2,4-dichloro derivative favors a similar conformation, the C—H bond lying *cis* to the ring chlorine atom. In contrast to the long-range proton-proton couplings, the longrange proton-fluorine couplings are intrinsically sensitive to substituent effects from the ring chlorine atoms.

La synthèse du fluorure de benzyle et de ses dérivés -2,6, -3,5, -3,4 et -2,4 dichlorés est suivie de l'analyse de leurs spectres de résonance magnétique du proton. Les constantes de couplage à longue distance sont très cohérentes avec une barrière de rotation autour de la liaison carbone-carbone sp²-sp³ dans le fluorure de benzyle, inférieure à 500 cal/mol; elles sont en accord semiquantitatif avec les résultats d'un calcul théorique de type *ab initio*. Le dérivé -2,6 dichloré présente une conformation dans laquelle la liaison C—H de la chaine latérale se trouve dans le plan du cycle aromatique. Le dérivé -2,4 dichloré favorise une conformation similaire, la liaison C—H se trouvant dans une position *cis* par rapport à l'atome de chlore du cycle. Par apposition aux constantes de couplage à longue distance proton-proton, les constantes de couplage à longue distance proton-fluore sont intrinsèquement sensibles aux effets de substitution des atomes de chlore du cycle. [Traduit par le journal]

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Introduction

The long-range coupling constants between ring and methyl protons in toluene (1, 2), between ring fluorine nuclei and methyl protons in fluorotoluene derivatives (3, 4), and between ring protons and fluorine nuclei in benzotrifluoride (5) have been discussed in terms of σ and π electron contributions to the coupling mechanisms. The coupling over six bonds between protons, ${}^{6}J_{p}^{H,CH_{3}}$, and between ring fluorine nuclei and methyl protons, ${}^{6}J_{p}^{F,CH_{3}}$, are transmitted by a π electron mechanism (2, 6). The corresponding couplings over four and five bonds have substantial σ electron contributions. In toluene derivatives, the side-chain proton ring proton coupling constants are highly stereospecific and relatively insensitive to the presence of ring substituents. These characteristics make them useful probes into the conformational preferences of these compounds. On the other hand, the couplings between side-chain fluorine nuclei and the ring protons in benzo-

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trifluoride derivatives display a substantial dependence on substituents (5). In addition, little is known about their conformational dependence. In this paper such long-range couplings are measured in benzal fluoride and four of its derivatives containing two chlorine atoms as ring substituents, 1-5.



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Product	Reactants (mmol)			Con		
	Aldehyde	SF ₄	BF3	Time (h)	Temp. (°C)	Yield (%)
1	31.3	63.2	_	6	150	80
2	15.6	31.6	_	10	150	< 5
	15.7	37.6	4.8	16	120	> 95
3	15.7	34.2	4.5	22	120	> 95
4	15.6	33.5	—	16	120	70
5	15.6	33.1	_	16	120	50





It turns out that the long-range coupling constants are best interpreted in terms of almost free rotation about the sp^2-sp^3 carbon-carbon bond in benzal fluoride. A ground state conformation in which the C—H bond of the side chain lies in a plane perpendicular to the aromatic ring can be ruled out.

Experimental

Synthesis

Fluorination of the corresponding aldehydes (Aldrich) gave the benzal fluorides (7). Sulfur tetrafluoride (Matheson) was handled in a metal vacuum system and was condensed into a 75-cc stainless steel pressure reaction vessel containing the aldehyde. In some cases, boron trifluoride (Matheson) was added as a catalyst. No attempt was made to optimize yields. Compound 3 was used without purification, while the others were distilled under reduced pressure in a closed system. Details of the reaction conditions are given in Table 1. Highly characteristic p.m.r. spectra, particularly for the methine proton, left no doubt as to the identity of the products.

Proton Magnetic Resonance Spectra

Thoroughly degassed samples (freeze-pump-thaw) contained small amounts of tetramethylsilane as an internal reference. The solvents are given below. Spectral calibrations were performed on a HA100D spectrometer in the frequency sweep mode at sweep rates of 0.01 or 0.02 Hz/s and at a sweep width of 1 Hz/cm. Double resonance experiments (8) on 3, 4, and 5 gave the signs of the long-range coupling relative to those of the couplings between fluorine and proton. Two different samples of 1 in C_6D_6 were calibrated in order to check the analysis of their complex spectra.

A solution of 2 in toluene- d_8 was cooled to below -100 °C but no evidence for slow rotation on the n.m.r. time scale was found. The spectral characteristics implied an upper limit of 8 kcal/mol to the free energy barrier to internal rotation about the C—C bond.

Results and Discussion

Spectral Analysis

The spectra of 2-5 approach first order and were analyzed using the computer program LAME (9). The 8-spin spectrum of 1 was rather complex and was analyzed in the iterative and noniterative modes of LACX (10). Spectral parameters were varied over generous ranges in a series of simulations to ensure that only the reported values gave a reasonable reproduction of the observed spectrum. A few impurity peaks caused minor difficulties; however, two different samples yielded almost identical parameter sets. In Fig. 1 the aromatic region of the spectrum of 1 is displayed, together with the calculated spectrum. The latter is obtained with the parameters given in column 2 of Table 2. All parameters except the shift of the methine proton, the shift of the fluorine nuclei, and $^{2}J^{H,F}$ were allowed to vary in the final iterations (for the other spectrum of 1 only the shift of fluorine was not allowed to vary). Of the 509 transitions of the aromatic protons having intensities greater than 0.01, 276 were assigned. Multiple near-degeneracies precluded more assignments. The r.m.s. deviation of calculated from observed transitions was 0.017 Hz; the standard deviations were very small, being as large as 0.007 Hz only for ${}^{6}J_{p}^{H,H}$ and ${}^{6}J_{p}^{H,F}$. The correlation coefficients were all less than 0.2 except that the shifts of the ortho and meta protons were correlated by 0.28, and ${}^{3}J^{H_{2},H_{3}}$ was correlated to each of these shifts by 0.42.

The final spectral parameters for all compounds are given in Table 2.



Fig. 1. The ring proton magnetic resonance spectrum at 100 MHz of a 15 mol % solution of benzal fluoride in benzene- d_6 . The spectrum calculated with the parameters in Table 2 is shown below the observed spectrum. The experimental traces at the extremes of the figure were taken at higher gain. Some impurity peaks occur in the extreme high-field part of the observed spectrum in the region of 694-697 Hz.

Parameter	1†	1†	2†	3‡	4†	5 §
V2	719.71	720.39		730.36		714.26
V3	702.98	703.68	678.03		696.73	-
V4	706.10	706.82	650.71	737.23		_
ν <u>s</u>	702.98	703.68	678.03		677.47	695.25
٧6	719.71	720.39	—	730.36	711.42	675.46
να	618	619.18	706.28	645.71	654.01	596.43
2ЈН, F	56.5	56.44	53.00	56.05	54.76	56.01
³ Ј ₀ н,н	7.80[2,3]	7.80	8.13		8.42	8.29
	7.54[3,4]	7.52	-	_		
4 <i>J</i> ^{н,н}	1.26[2,4]	1.26	_	1.89	2.05	2.05
	1.88[2,6]	1.89	_		—	
	1.31[3,5]	1.31				_
⁵ Ј _р н,н	0.63	0.63		<u> </u>	0.36	0.37
$4J_o^{H,CH_{\alpha}}$	-0.47	-0.46		-0.49	-0.45	-0.45[2]
${}^{5}J_{m}^{H,CH_{\alpha}}$	0.26	0.26	0.24	-	0.00[3] 0.48[5]	0.31
${}^{6}J_{p}^{H,CH_{\alpha}}$	-0.24	-0.25	-0.01	-0.28		
4 <i>J</i> ₀ ⁻ H,CF	-1.16	-1.17	-	-1.02	-0.91	-1.08[2] -1.08[6]
${}^{5}J_{m}^{H,CF}$	0.92	0.92	1.06	—	1.20[3]	0.95
б _{Јр} н,сғ	-1.16	-1.12	-1.25	-0.95		

TABLE 2. The chemical shifts* and coupling constants in Hz of benzal fluoride and some dichloro derivatives

*In Hz at 100 MHz to low field from internal TMS. †Approximately 15 mol % in C₆D₆. ‡Approximately 10 mol % in CS₂. §Approximately 20 mol % in C₆D₆. Not iterated on these parameters.

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Long-range Couplings to the a Proton, Conformational Preferences, and Rotational Barriers

(a) Over Five Bonds, ${}^{5}J_{m}^{H,CH_{\alpha}}$

In 2,6-dichlorobenzal chloride the conformation analogous to 2 is about 15 kcal/mol more stable (11) than the high energy conformation (12) in which the C-H bond of the dichloromethyl group lies in a plane perpendicular to the aromatic ring. The long-range coupling ${}^{5}J_{m}^{H_{3},CH_{\alpha}}$ is 0.50 \pm 0.02 Hz in that compound while ${}^{5}J_{m}^{H_{5},CH_{\alpha}}$ is less than 0.05 Hz. In 2 the barrier to rotation is probably less than 8 kcal/mol (see Experimental) and rapid conformational isomerism about the sp²-sp³ carboncarbon bond could lead to the observed coupling of 0.24 Hz = $({}^{5}J_{m}{}^{H_{5},CH_{\alpha}} + {}^{5}J_{m}{}^{H_{3},CH_{\alpha}})/2$. In 4 one observes ${}^{5}J_{m}{}^{H_{5},CH_{\alpha}}$ as 0.48 Hz while ${}^{5}J_{m}{}^{H_{3},CH_{\alpha}}$ is unobservable, implying that 4 exists predominantly as 4a. In 1 the coupling is 0.26 Hz, again suggesting equal populations of the isomers corresponding to conformation 1. In 5 the observed coupling of 0.31 Hz then would suggest that 5a is populated to an extent of about 60%, this conformation having a somewhat smaller dipole moment than 5b, i.e., a larger separation of negative halogen centers. These conclusions assume a negligible substituent dependence on ${}^{5}J_{m}^{H,CH_{\alpha}}$, in line with the data on the 2,4,6-trichlorobenzal chloride (12) and the 2,4,6-tribromobenzal chloride (13).

The ${}^{6}J_{p}^{H,CH_{\alpha}}$ values are interpreted below in terms of an almost free rotation about the C—C bond in 1, 3, and 5 (but not in 2). The question therefore arises whether the five-bond couplings are also consistent with the latter model.

Calculations on ${}^{5}J_{m}^{\text{H},\text{CH}_{3}}$ in toluene (2) suggest that the coupling is dominated by a σ electron mechanism which has a $(1 - \cos \theta)/2$ dependence and that a smaller contribution to the coupling originates in a π electron mechanism, depending on $\sin^{2} \theta$. From the measurement (6) of ${}^{6}J_{m}^{\text{CH}_{3},\text{CH}_{3}}$ in a *m*-xylene derivative, it was suggested that the π contribution was given by 0.38 $\sin^{2} \theta$ in Hz. If, then, the π contribution to ${}^{5}J_{m}^{\text{H},\text{CH}_{\alpha}}$ in benzal fluoride is reduced in proportion to ${}^{6}J_{p}^{\text{H},\text{CH}_{\alpha}}$, *i.e.*, by $(-0.52 \times 0.38)/(-1.24)$, one may write

[1]
$${}^{5}J_{m}^{\text{H,CH}_{\alpha}} = {}^{5}J^{\sigma} + {}^{5}J^{\pi}$$

= 0.48 (1 - cos θ)/2 + 0.15 sin² θ

For free rotation, an average from 0 to 2π

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radians yields ${}^{5}J_{m}^{H,CH_{\alpha}} = 0.24 + 0.07 = 0.31$ Hz. In other words, the π contribution raises ${}^{5}J_{m}^{H,CH_{\alpha}}$ somewhat from the value expected for rapid flips between coplanar conformations of type 1 or 2. The calculated value of 0.31 Hz is a little larger than the 0.26 Hz observed in 1 but equal to that in 5. The difference from 1 is too small to vitiate the model of nearly free rotation.

For 4 one may have an oscillation up to 30° about the C—C bond for conformation 4*a* and find that the calculated values are still within experimental error of the observed parameters, *i.e.*, eq. 1 averaged between $-\pi/6$ and $\pi/6$ yields 0.03 Hz (coupling to H₃) and yields 0.48 Hz when averaged between $5\pi/6$ and $7\pi/6$ (coupling to H₅). The free rotation model for 1 is, therefore, not disproved by the data on 4.

(b) Over Six Bonds, ⁶J_p^{H,CH_α}, and Barrier to Rotation

In 1 the barrier to rotation about the C-C bond may be rather small. Ab initio calculations (14) indicate 1 as more stable by 180 cal/mol than the form where the C-H bond lies in a plane perpendicular to the ring plane. Experimental data are unavailable. Such a low twofold barrier is only an order of magnitude larger than the sixfold barrier in toluene (15). If it is correct, then at room temperature the population of 1 is only 1.35 times the population of the perpendicular form. Classically, such a low barrier would entail large amplitudes of oscillation about the C-C bond in both 1 and the perpendicular conformation. Evidence for a substantial oscillation, at least in 1, comes from the ${}^{6}J_{\pi}^{H,CH_{\alpha}}$ values in 1, 2, and 3. Because this coupling is transmitted by a mechanism (2) in which $\sigma -\pi$ interaction occurs between the C-H_n bond and the π electron system of the aromatic ring, it has a $\sin^2 \theta$ dependence where θ is the angle between the plane of the aromatic ring and the plane containing the C— H_{α} bond. In 2 the coupling is effectively zero because θ is 0° and oscillations about this value of up to 15° will not increase the magnitude of the coupling significantly (16, 17). Quantum mechanically, a barrier to rotation in 2 of about 2 kcal/mol guarantees the same conclusion (17).

Now, in 1 and 3 the value of ${}^{6}J_{p}^{H,CH_{\alpha}}$ is -0.26 ± 0.02 Hz, indicating a substantial amplitude of oscillation in conformation 1 or a barrier lower than 2 kcal/mol. Unfortunately, no value of ${}^{6}J_{p}^{H,CH_{\alpha}}$ is available for $\theta = 90^{\circ}$ for the diffuoro-

and the second sec

methyl group. For *free* rotation, $\langle \sin^2 \theta \rangle = 0.5$, so that a *maximum* value of ${}^6J_p{}^{\text{H,CH}_{\alpha}}(\theta = 90^\circ)$ would then be -0.52 ± 0.04 Hz. For the methyl group, the corresponding value is -1.24 Hz, while for the fluoromethyl group it is -0.64 Hz (16). For CH₂X groups the σ - π interaction decreases in magnitude in a roughly linear fashion as the electronegativity of X increases (16), so that a further decrease might well occur in going from CH₂F to CHF₂.

The first fluorine atom substituent decreases ${}^{6}J_{p}^{\text{H,CH}_{\alpha}}$ by a factor of two from its value in the methyl group. If, in fact, the second fluorine atom again halves ${}^{6}J_{p}^{\text{H,CH}_{\alpha}}$ ($\theta = 90^{\circ}$), *i.e.*, to about -0.32 Hz, then the observed values of -0.26 ± 0.02 Hz in 1 and 3 are in agreement with neither a free rotation model nor a ground state conformation 1. Rather one would need a perpendicular conformation with a substantial oscillation of near 30° about the C—C bond.

It is probably reasonable that substitution by a second fluorine atom does not have as large an effect on ${}^{6}J_{p}^{H,CH_{\alpha}}(\theta = 90^{\circ})$ as does substitution by the first fluorine atom into the methyl group. Then the value of -0.52 Hz above appears adequate as an estimate and is in agreement with the quantum mechanical model of Stone and Maki (17) for a barrier of 180 cal/mol, this value being hardly distinguishable from free rotation. In this model, if 1 is the ground state with a barrier to rotation of as much as 1 kcal/mol, the experimental value of -0.26 Hz implies a ${}^{6}J_{p}^{H, CH_{\alpha}}(\theta = 90^{\circ})$ of about -1.3 Hz, even larger than for the methyl group itself. Even a barrier of 0.5 kcal/mol entails a value of -0.74, greater in magnitude than the -0.64 Hz derived for the fluoromethyl group (16).

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The present measurements, therefore, indicate a barrier of less than 0.5 kcal/mol for the barrier to internal rotation in benzal fluoride and also imply that the ground state is **1**. A microwave measurement of the barrier would be of interest, even though it may not indicate the ground state conformation if the barrier is very small.

(c) Coupling Over Four Bonds, ${}^{4}J_{o}^{H,CH_{\alpha}}$

To within experimental error, this coupling is the same in the four compounds where it occurs and since 4 exists predominantly in form 4a, it is apparently not suited to stereochemical deductions. The coupling presumably contains substantial contributions from both σ and π electrons (2, 6) and therefore its value need not vanish when the C—H_a lies in the plane of the aromatic ring. It would be useful to know whether ${}^{4}J_{o}^{H,CH_{a}}$ has different values at $\theta = 0$ and 180°. Therefore, MO-INDO-FPT and MO-CNDO/2-FPT calculations were carried out on benzal fluoride.

(d) INDO and CNDO/2 Calculations of ${}^{4}J_{o}^{H,CH_{\alpha}}, {}^{5}J_{m}^{H,CH_{\alpha}}$ and ${}^{6}J_{p}^{H,CH_{\alpha}}$

These were performed on an IBM 360/65 computer in a manner described in detail for other molecules (2). Up to a hundred iterations were performed to achieve convergence in the coupling constants to about 10^{-3} Hz. The finite perturbation (18) was applied to the α proton for a standard geometry (20) and the angle was varied at intervals of 10 to 15°. Convergence was not obtained for some values of θ , which is defined by **6**. The computed couplings are given in Table 3.



(i) Over Four Bonds, ${}^{4}J_{o}^{H,CH_{\alpha}}$

In Fig. 2 the computed ${}^{4}J_{o}^{H,CH_{\alpha}}$ values are plotted as a function of the angle θ . The CNDO/2 predictions are clearly in disagreement with experiment, as expected if they do not take the $\sigma-\pi$ mechanism into account (19). INDO predicts that the coupling is -0.3 Hz when $\theta = 180^{\circ}$ and 0.13 Hz when $\theta = 0^{\circ}$, suggesting 4a as the conformation for 4, particularly if a sizeable oscillation occurs about the C—C bond.

The shape of the computed curve, with its maximum magnitude near $\theta = 90^{\circ}$, implies a large π contribution to ${}^{4}J_{o}^{\text{H,CH}_{\alpha}}$ similar to that observed and calculated (2) for toluene. The average value over all angles in Table 3 is -0.48 Hz, in fortuitous quantitative agreement with the observed numbers for 1 and 3. Thus, the INDO computations of ${}^{4}J_{o}^{\text{H,CH}_{\alpha}}$ agree with almost unhindered rotation about the C--C bond in 1 and 3. For a large barrier to rapid rotation between identical forms 1, INDO would indicate substantially different values in 1 and 4, contrary to experiment.

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TABLE 3. Computed long-range coupling constants in Hz in benzal fluoride

θ* (deg)	${}^{4}J_{o}^{H,CH_{\alpha}}$		⁵ J	H, CHα	⁶ J _p ^{H,CHα}	
	INDO	CNDO/2	INDO	CNDO/2	INDO	CNDO/2
5	0.112	0.276	0.038	0.075	-0.020	0.003
15	0.063	_	0.066	_	-0.071	
30	-0.090	0.265	0.156	0.042	-0.226	0.003
45	-0.315		0.290		-0.440	
60	-0.561	0.215	0.448	0.003	-0.653	0.002
75	-0.768	_	0.605		-0.808	
85	-0.858	0.166	0.700	0.049	-0.858	0.002
95	-0.899	0.151	0.781	0.097	-0.858	0.002
105	-0.890	_	0.848	—	-0.808	
120	-0.793	0.126	0.918	0.286	-0.653	0.002
135	-0.632	_	0.953	_	0.440	 -
150	-0.463	0.113	0.959	0.535	-0.226	0.003
165	-0.337		0.953	_	-0.071	
175	-0.297	0.112	0.950	0,638	-0.020	0.003

*The angle θ is defined by 6 in the text and has the C—H_{α} bond in the plane of the ring and *cis* to the *ortho* proton when $\theta = 0^{\circ}$.



FIG. 2. The calculated coupling over four bonds between the α proton and the orthoring protons as a function of the rotational angle θ in benzal fluoride. $\theta = 0^{\circ}$ refers to the conformation in which the C-H_a bond lies in the plane of the ring and cis to the ortho proton.

(*ii*) Over Six Bonds, ${}^{6}J_{p}^{H,CH_{\alpha}}$ The INDO coupling in Table 3 closely follows ${}^{6}J_{p}^{\text{H,CH}_{\alpha}} = 0.87 \times \sin^{2} \theta$ while the CNDO/2 result never rises above 0.0034 Hz, clearly indicating a π electron mechanism. The value of -0.87 Hz at $\theta = 90^{\circ}$ is an overestimate in view of the experimental value of -0.64 Hz for the fluoromethyl group, discussed in a previous section, where a free rotation model implied -0.52 Hz at $\theta = 90^{\circ}$ for the diffuoromethyl group. If the calculated value were actually correct, simple averaging suggests an oscillation by 45° about the conformation 1 will also lead to an observed value of -0.26 Hz for ${}^{6}J_{p}^{H,CH_{\alpha}}$. Such a large oscillation implies a rather small barrier to internal rotation.

(iii) Over Five Bonds, ${}^{5}J_{m}^{H,CH_{\alpha}}$

The INDO and CNDO/2 values are plotted in Fig. 3. For toluene (2), benzaldehyde (21), and styrene (22), INDO substantially overestimates the magnitude of a five-bond coupling from an α proton. A similar situation exists for benzal fluoride, as can be seen in Fig. 3 where the values predicted by eq. 1 are also plotted. Comparison with the CNDO/2 curve indicates the π electron contribution to ${}^{5}J_{m}^{\text{H,CH}_{\alpha}}$ included in eq. 1, this contribution being substantially smaller than that clearly contained in the INDO curve. The experimental values in Table 2 suggest that neither the CNDO/2 nor the INDO curves are quantitatively correct. Reduction of the computed INDO values by a factor of two would produce a θ dependence of ${}^{5}J_{m}^{H,CH_{\alpha}}$ in



FIG. 3. The computed couplings over five bonds between the α proton and the ring proton as a function of rotational angle θ are plotted as solid lines. The dashed line refers to the couplings calculated from eq. 1 of the text. $\theta = 0^{\circ}$ refers to the conformation in which the C-H_a bond lies in the plane of the ring and *cis* to the meta proton.

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agreement with a free rotation model as well as with eq. 1.

Long-range Coupling from the Fluorine Nuclei (a) Over Six Bonds, ${}^{6}J_{p}^{H,CF}$

In benzal fluoride ${}^{6}J_{p}^{H,CF}$ is -1.14 Hz. If the C-H, bond lay in a plane perpendicular to the aromatic ring, the C-F bond would lie at 60° from the perpendicular, so that ${}^{6}J_{p}^{H,CF}$ ($\theta = 90^{\circ}$ for F) would have a value of $-1.14/\sin^2 30^\circ =$ -4.56 Hz. In benzotrifluoride, however, the corresponding value is -1.28 Hz (5) and is -2.43 Hz in 2,6-dichlorobenzyl fluoride (23), *i.e.*, ${}^{6}J_{p}^{H,CF}$ decreases substantially in magnitude as more electronegative fluorine atoms are substituted into the methyl group (similar to the decrease in magnitude of ${}^{6}J_{p}^{H,CH_{\alpha}}$ on going from CH₃ to CHF₂ groups). Consequently, it is highly unlikely that the stable conformation of benzal fluoride is one in which the C— H_{α} bond lies perpendicular to the ring.³

On the other hand, if 1 is by far the most stable conformation of benzal fluoride it follows that ${}^{6}J_{p}^{H,CF}$ at 90° (C—F perpendicular to ring) is -2.28 Hz for benzal fluoride, -1.27 Hz for 3,5-dichlorobenzal fluoride, and -1.67 Hz for 2,6-dichlorobenzal fluoride (sin² $60^{\circ} = 0.75$). A substantial ring-substituent effect on ${}^{6}J_{n}^{H,CF}$ is clearly present. However, it is improbable that the chlorine atoms in the 3 and 5 positions should have a larger effect than in the 2 and 6 positions (because they are known not to affect ${}^{6}J_{p}^{H,CH_{3}}$). Therefore, the substituent effect must occur at the site where the C-F bonds undergo σ - π interaction with the π system of the ring, because the σ - π interaction at the C—H bond in the para position of the ring is no doubt much the same for 3,5-dichlorobenzal fluoride and 3,5-dichlorotoluene.

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Now, if almost free internal rotation occurs

³Our INDO and CNDO/2 calculations suggest the perpendicular form as more stable than the form 1 by 1.5 and 1.9 kcal/mol, respectively, contrary to the *ab initio* calculations (14). It appears likely that the reason for the error in the former lies in the fact that they favor more highly connected conformations, the two C—F bonds lying at 30° from the plane of the ring and, therefore, bringing the fluorine atoms closer to the ring atoms than when the C—H_a lies in the plane of the ring. Such an effect is particularly noticeable for calculations on carbonium ions (24). Of course, a proper optimization of geometry for each conformation of 1 may change substantially the energy calculated by both methods.

about the C—C bond (180 cal/mol barrier (14)), the values of ${}^{6}J_{p}^{H,CF}$ at 90° (C—F perpendicular to ring) become -2.28 Hz for benzal fluoride, -1.90 Hz for the 3,5-dichloro derivative, and -1.76 Hz for the 2,6-dichloro derivative (because $\langle \sin^{2} \theta \rangle = 0.5$ for the first two, while the last compound exists in form 2). The ringsubstituent effect now increases in magnitude as the chlorine atoms more closely approach the difluoromethyl group, and there occurs a steady progression in the derived J values.⁴

The six-bond coupling to fluorine in benzal fluoride is therefore best interpreted in terms of an almost free rotation of the difluoromethyl group about the C—C bond.

(b) Over Five Bonds, ${}^{5}J_{m}^{H,CF}$

In 4, ${}^{5}J_{m}^{H,CF}$ is 0.57 Hz to H₅ and 1.20 Hz to H₃, indicating form 4*a* if ${}^{5}J_{m}^{H,CF}$ follows an equation similar to eq. 1. Such an assumption implies two equations in ${}^{5}J_{m}^{H,CF}$. These yield a σ electron contribution of 1.26 Hz at $\theta = 180^{\circ}$ (*trans*), 0.00 Hz at $\theta = 0^{\circ}$, and 0.34 Hz for the π electron contribution to ${}^{5}J_{m}^{\text{H,CF}}$. But a ringsubstituent effect is probably present here also so that a direct comparison with the other compounds is difficult. Thus, in 2 the average coupling over five bonds is 1.06 Hz, almost 0.2 Hz higher than the 0.89 Hz obtained from the average of the two couplings in 4. Yet this average is nearly equal to the 0.92 Hz observed in 1. In the absence of ring-substituent effects on ${}^{5}J_{m}^{H,CF}$, this equality would indicate that benzal fluoride exists in conformation 1. If, then, the chlorine atoms reduce the π contribution to ${}^{5}J_{m}^{H,CF}$ in 2 (as they apparently do for ${}^{6}J_{p}^{H,CF}$), they must increase the σ electron contribution to this coupling in 2. In order to reconcile all these observations with an "almost free rotation" in benzal fluoride, assume that the π electron contribution to ${}^{5}J_{m}^{H,CF}$ has the same ratio to ${}^{6}J_{p}^{H,CF}$ as for the corresponding couplings in toluene (2), namely, -1/3. One has (2.28)/ $(3 \times 2) = 0.38$ Hz for ${}^{5}J^{\pi}$ for free rotation, leaving 0.54 Hz as ${}^{5}J^{\sigma}$. The latter is indeed smaller than the 0.63 Hz derivable from the 1.26 Hz deduced for ${}^{5}J^{\sigma}$ in 4, as expected if the ortho ring-substituent increases ${}^{5}J^{\sigma}$; an increase being necessary to explain the value of ${}^{5}J_{m}^{H,CF}$ in 2, as

⁴Hence the value of ${}^{6}J_{p}{}^{\text{H,CF}}$ (at 90°) of -2.43 Hz in 2,6-dichlorobenzyl fluoride (23) is not necessarily the same as its value in benzyl fluoride.

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was indicated above. Although the asymmetry in the substitution pattern in 4, as compared to 2, does not encourage quantitative comparisons once a ring-substituent effect on both the π and σ electron contributions to ${}^{5}J_{m}^{H,CF}$ is admitted, it is clear that the values of this coupling for the compounds in Table 2 do not disprove the "almost free rotation" model for benzalfluoride.

(c) Over Four Bonds, ${}^{4}J_{o}^{H,CF}$

A decrease in magnitude of this coupling as chlorine atoms are introduced on the ring (Table 2) is again explicable in terms of a ring-substituent effect on both σ and π contributions to ${}^{J_o}_{J_o}^{H,CF}$ and cannot be used to contradict the "almost free rotation" model. Note that the magnitudes of ${}^{4J_o}_{J_o}^{H,CF}$ and ${}^{6J_p}_{P}^{H,CF}$ are nearly equal in a given compound and that substitution patterns can hardly be deduced from their comparison.

Conclusions

The long-range nuclear spin-spin couplings from the side-chain nuclei to the ring protons in benzalfluoride are best interpreted when the barrier to rotation about the sp^2-sp^3 carboncarbon bond is less than 500 cal/mol. This result is consistent with an *ab initio* molecular orbital calculation which finds the conformation in which the C—H bond of the sidechain lies in the plane of the ring to be 180 cal/mol more stable than the conformation in which the C—H bond lies in a plane perpendicular to the ring. In contrast to the long-range proton-proton coupling constants, the long-range proton-fluorine couplings are sensitive to substituent effects from chlorine atoms in the ring.

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- 1. M. P. WILLIAMSON, R. J. KOSTELNIK, and S. M. CASTELLANO. J. Chem. Phys. 49, 2218 (1968).
- 2. R. WASYLISHEN and T. SCHAEFER. Can. J. Chem. 50, 1852 (1972).
- 3. D. J. BLEARS, S. S. DANYLUK, and T. SCHAEFER, J. Chem. Phys. 47, 5037 (1967).
- 4. R. WASYLISHEN and T. SCHAEFER. Can. J. Chem. 49, 94 (1971).
- R. J. KOSTELNIK, M. P. WILLIAMSON, D. E. WIS-NOSKY, and S. M. CASTELLANO. Can. J. Chem. 47, 3313 (1969).
- 6. C. J. MACDONALD and W. F. REYNOLDS. Can. J. Chem. 48, 1002 (1970).
- 7. W. C. SMITH. Angew. Chem. Int. Ed. 1, 467 (1962).
- 8. W. A. ANDERSON and R. FREEMAN, J. Chem. Phys. 37, 2053 (1962); 39, 806 (1963).
- 9. C. W. HAIGH and J. M. WILLIAMS. J. Mol. Spectrosc. 32, 398 (1969).
- 10. C. W. HAIGH. Private communication.
- 11. T. SCHAEFER, R. SCHWENK, C. J. MACDONALD, and W. F. REYNOLDS. Can. J. Chem. 46, 2187 (1968).
- I2. B. J. FUHR, B. W. GOODWIN, H. M. HUTTON, and T. SCHAEFER. Can. J. Chem. 48, 1558 (1970).
- 13. J. PEELING, T. SCHAEFER, and C. M. WONG. Can. J. Chem. 48, 2839 (1970).
- 14. W. J. HEHRE, L. RADOM, and J. A. POPLE. J. Am. Chem. Soc. 94, 1496 (1972).
- 15. H. RUDOLPH, H. DREIZLER, A. JAESCHKE, and P. WENDLING. Z. Naturforsch. 22a, 940 (1967).
- A. F. JANZEN and T. SCHAEFER. Can. J. Chem. 49, 1818 (1971).
- 17. E. W. STONE and A. H. MAKI, J. Chem. Phys. 37, 1326 (1962).
- J. A. POPLE, J. W. MCIVER, JR., and N. S. OSTLUND. J. Chem. Phys. 49, 2960, 2965 (1968).
- J. A. POPLE and D. L. BEVERIDGE. Approximate molecular orbital theory. McGraw-Hill Book Company, New York, N.Y. 1970.
- 20. J. A. POPLE and M. S. GORDON, J. Am. Chem. Soc. 89, 4253 (1967).
- 21. R. WASYLISHEN and T. SCHAEFER. Can. J. Chem. 49, 3216 (1971).
- 22. M. BARFIELD, C. J. MACDONALD, I. R. PEAT, and W. F. REYNOLDS. J. Am. Chem. Soc. 93, 4195 (1971).
- 23. T. SCHAEFER, C. M. WONG, and K. C. TAM. Can. J. Chem. 47, 3688 (1969).
 - V. BUSS, P. VON R. SCHLEYER, and L. C. ALLEN. Topics Stereochem. 7, 253 (1973).

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