Barrier to Internal Rotation in 2,6-Dichlorobenzal Iodide and some α, α'-m-Xylyl Halides. Experimental Evidence for the Transition State Conformation in Benzal Halides

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The barriers to internal rotation in the α, α' -di-X-2,4,5,6-dichloro-*m*-xylenes (X = Cl, Br, I) are determined by proton magnetic resonance bandshape analyses. Their magnitudes are experimental evidence for the calculated conformation of the activated rotational state of the benzal halides, in which the C—H bond of the side chain is predicted to lie in a plane perpendicular to the aromatic nucleus. The synthesis and the barrier to rotation in 2,6-dichlorobenzal iodide are reported.

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On a déterminé, par l'analyse de la forme des bandes de r.m.n., les barrières à la rotation interne dans les α, α' -di-X dichloro *m*-xylènes-2,4,5,6. On déduit des valeurs observées que les molécules existent dans la conformation calculée pour l'état rotationnel activé des halogénures de benzal dans lesquels le lien C—H de la chaîne latérale serait dans un plan perpendiculaire au noyau aromatique. On rapporte la synthèse et les barrières à la rotation dans l'iodure de dichloro-2,6 benzal. [Traduit par le journal]

Introduction

A recent analysis (1) of the long-range spinspin coupling constants in benzal fluoride and its dichloro derivatives shows that its ground state conformation is 1 and that the barrier to internal rotation is substantially less than 0.5 kcal/mol, in agreement with an *ab initio* molecular orbital prediction of 0.18 kcal/mol (2) for the barrier and



 $\mathbf{Y} = \mathbf{H}, \mathbf{Cl}, \mathbf{Br}$

of **1** as the low energy form. As the size of the substituents X and Y in **1** increases, the barrier naturally rises (3) until for 2,6-dichlorobenzal iodide the free energy of activation, ΔG^{\pm} , becomes $21.0_5 \pm 0.1_0$ kcal/mol near 377 °K (see below).

All compounds 1 have the indicated ground state conformation, as have those in which two or three $CHCl_2$ groups are spaced by at least one ring halogen substituent (4). Molecular models

and approximate potential energy calculations (5) suggest a high energy conformation, 2, in which a C—X bond eclipses the C—Y bond.



More accurate classical calculations (3, 6) predict 3 as the high energy form and give reasonably



good agreement with the observed barriers to internal rotation.¹ However, the computational

 1 CNDO/2 and INDO computations (7*a*) in this laboratory using the geometries predicted by the classical model, yield **3** as the *low* energy conformation. complexities demand some approximations (6) and consequently it seems desirable to obtain experimental evidence for 3 as the transition state in the internal rotation process. This can be done by the following indirect approach.

Of course, the high energy form is not observable. However, if **3** is the transition state for the CHX_2 group, the eclipsed conformation **2** being of lower energy, it follows that the benzyl halide, **4**, whose transition state is the eclipsed



conformation, 5, must have a *considerably* lower barrier to internal rotation than do the benzal halides. This conclusion is reasonable because the calculations predict that $6 (0^{\circ}, 60^{\circ}$ interaction) has a substantially lower potential energy than 7 ($30^{\circ}, 30^{\circ}$ interaction). Furthermore, a



 60° , 60° interaction as in 1 represents a near-zero potential energy (see calculations below), so that the eclipsed form 5 for the benzyl halide will hardly be of higher energy than 6 for the benzal halide.

The barrier in the symmetrical benzyl halide, 4, is not accessible to line-shape fitting methods. Therefore the more complex compounds 8, 9, 10,



were prepared. Insofar as the CH_2X groups within a given molecule can take on independent orientations, the protons in different methylene groups (8 and some forms of 10) or within the same methylene group (9 and some forms of 10) need not be isochronous. Thus, for 9 the two forms 11 and 12 can display two distinct $[AB]_2$



proton magnetic resonance spectra. Rapid rotation of the CH_2X groups on the time scale defined by the extent of the anisochronicity within one $[AB]_2$ spectrum *and* between the two $[AB]_2$ spectra leads to a single peak A_4 and the line shape at intermediate rotational rates contains an extractable rate constant.

For reasons described below, only ΔG^{\dagger} could be found and that only for 9 (X = Cl, Br, I). Yet the results suffice as an indirect demonstration of the conformation of the rotational transition state in the benzal halides. In addition, the barrier to rotation in the 2,6-dichlorobenzal iodide is measured and calculated.

Experimental

Preparation of Compounds

(a) 2,6-Dichlorobenzal Iodide (7b)

2,6-Dichlorobenzaldehyde (10 g), 20 ml of hydrazine hydrate, and 50 ml of CCl₄ were refluxed for 1.5 h. On cooling, white need'es precipitated and the mixture was filtered after the addition of 50 ml of H₂O. The needles were washed with H₂O, dried by suction, and were added to 30 ml of CCl₄ and 70 ml of N(CH₃)₃. On addition of 25 g of I₂ in ether, a gas evolved rapidly. The solution was washed with 100 ml volumes of 5% aqueous Na₂S₂O₃, 3 N HCl, 5% aqueous K₂CO₃, filtered, the solvent boiled off, leaving a red oil which was extracted twice with 50 ml portions of absolute ethanol. The product was a brown powder.

(b) The α, α' -Dihaloxylene Derivatives

Compounds 8 (X = Cl) and 9 (X = Cl) were obtained from Aldrich; compound 10 (X = Cl) was prepared from mesitylene (4). The bromine derivatives of 8, 9, and 10 (X = Br) were prepared by slow addition of an aqueous solution of KBr to boiling acetone solutions of the corresponding chlorides. After refluxing for 2 h the solution was poured into water and the precipitate was collected and recrystallized from ethanol (for the bromine derivative

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Compound*	Melting point (°C)	Mol % (solvent)	Chemical shift [†] (p.p.m.)	
p-Cl	178–180	1 (toluene- d_8)	4.260	
<i>p</i> -Br	211-212	1 (toluene- d_8)	4.125	
p-I	> 300	Insoluble		
m-Cl	138-140	1 (toluene- d_8)	4.301	
<i>m</i> -Br	158-160	1 (toluene- d_8)	4.124	
m-I	180.5-181.5	1 (toluene- d_8)	4.051	
Mesityl-Cl	159-161	1 (CS ₂)	4.847	
Mesityl-Br	180-181	$1(CS_2)$	4.720	
Mesityl-I	219.5-221.5	$0.25 (CS_2)$	4.637	

TABLE 1. Physical characteristics of ring chlorinated α, α' -xylyl halides and $\alpha, \alpha', \alpha''$ -mesityl halides

**p*-Cl means $\alpha, \alpha', 2, 3, 5, 6$ -hexachloro-*p*-xylene, *m*-I means α, α' ,-diiodo-2,4,5,6-tetrachloro-

*Relative to internal tetramethylsilane at 32 °C.

of 10 the exchange was repeated four times, recrystallization from CCl_4).

For the iodine derivatives of 8, 9, and 10, acetone solutions of the chlorides were added to acetone solutions of NaI and the mixtures were poured into water. The precipitate was collected and recrystallized from CCl₄. Chemical shift and m.p. data for these compounds are collected in Table 1.

Proton Magnetic Resonance Spectra

(a) 2,6-Dichlorobenzal Iodide

A 7 mol% solution in 1,2,3-trichloropropane, containing a small amount of hexamethyldisilane, was not sealed for reasons of safety. Proton magnetic resonance spectra were calibrated on an HA100D spectrometer at sweep rates of 0.02 or 0.05 Hz/s. The homogeneity of the magnetic field was monitored by the appearance of those resonance peaks (methine and the two outer peaks of H₄ corresponding to $\alpha\alpha$ and $\beta\beta$ spin states of H₃ and H₅) whose width was independent of the exchange rate. Temperatures were measured as described previously (8). Fairly, rapid decomposition occurred above about 110 °C.

(b) The α, α' -Dihaloxylene Derivatives

Solutions of 9 (X = Br, I) (1 mol%) in toluene- d_8 , containing a very small amount of CH₂Cl₂ for monitoring magnet homogeneity and tetramethylsilane as a locking material, were used at temperatures down to -90 °C. For X = Cl, a 0.5 mol% solution in toluene- d_8 was used for reasons of solubility. No other suitable low-temperature solvent was found for 9.

For 8 (X = I) no solvent was found; but for 8 (X = Cl, Br) very dilute solutions in toluene- d_8 could be cooled to -80 °C. Some broadening of the spectral peak at -80 °C may have arisen, not from a rate process, but from partial precipitation of the solute.

The solubility of 10 (X = Cl, Br, I) at low temperatures was insufficient for spectral work.

Results and Discussion

2,6-Dichlorobenzal Iodide

(a) Spectral Parameters at Low Rotation Rates

Near ambient temperatures the rate of con-



FIG. 1. The proton magnetic resonance spectrum at 100 MHz and 50.6 °C of a 7 mol% solution of 2,6-dichlorobenzal iodide in 1,2,3-trichloropropane. The solution was undegassed and the chemical shift scale is in Hz to low field of internal hexamethyldisilane. The labelling refers to structure 13 of the text.

version from 13 to its superimposable mirror image 14 is low enough for observation of an ABCD proton spectrum at 100 MHz (see Fig. 1). The spectral parameters at 33.0 and 50.6 °C are given in Table 2 as obtained from the program LAME (9). To within experimental error the spin-spin coupling constants are temperature independent. The shift between H_A and H_B , whose Larmor frequencies define the sites between which exchange occurs, does not change over this temperature range. The resonance frequency of H_D is the same in 13 and 14 and therefore its peaks



do not broaden at intermediate exchange rates. The two outer peaks of H_c are not broadened by

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TABLE 2. Spectral parameters and free energies of rotational activation for 2,6-dichlorobenzal iodide, 7 mol % in 1,2,3-trichloropropane

		Value at			
Parameter	33.	0 °C	50.6 °C		
V _A *	732.24	(0.006)†	731.29 (0.005)		
$\nu_{\rm B}$	716.21	(0.006)	715.28 (0.006)		
vc	703.68	(0.007)	702.43 (0.006)		
$v_{\mathbf{D}}$	725.38	4 (0.007)	726.01 (0.005)		
${}^{4}J_{AB}$	1.28	(0.008)	1.27(0.007)		
${}^{3}J_{AC}$	8.07	(0.008)	8.10 (0.008)		
${}^{3}J_{\rm BC}$	8.12	(0.008)	8.11 (0.007)		
⁵ <i>J</i> _{AD}	0.54	0.54(0.008)			
⁵ J _{BD} §	-0.01	-0.01(0.008)			
6Jop 8	-0.02	(0,008)	-0.04(0.007)		
Root mean square er	or 0.01	0.0123			
Largest error	0.01	0.035			
Lines assigned	32	5	32		
		٨G	+		
T (°K)	k (s ⁻¹)	k (s ⁻¹) (kcal/			
366.5	2.25 ± 0.15	21.02 ±	0.08		
378.9	6.25 + 0.75	20.98 +	0.11		
390.2	11.5 ± 1.5	$21.16 \pm$	0.11		

*In Hz at 100 MHz to low field of internal hexamethyldisilane. Probable errors, to be multiplied by a factor of 3 to 5.

\$Not necessarily different from zero.

the rate process because they correspond to $\alpha\alpha$ and $\beta\beta$ states for H_A and H_B. These H_C peaks and the H_D peaks serve as convenient measures of the linewidth corrections, T₂, applicable to the exchange-broadened spectra.

(b) Free Energy of Activation (ΔG^{\dagger})

Decomposition occurs fairly rapidly above 110 °C. Exchange-broadened spectra were obtained at 93.3, 105.7, and 117.0 °C, coalescence occurring above 120 °C. Rate constants were obtained by matching complete spectral lineshapes with those calculated by the program DNMR2 (10, 11). Rate constants and ΔG^{\pm} values at the three temperatures are given in Table 2. The errors are the linearized relative statistical errors (12), including those arising from uncertainties in both the rate constants and in the temperatures. Slow decomposition occurred at temperatures above 90 °C, so that insufficient data could be collected for a reliable determination of ΔH^{\dagger} and ΔG^{\pm} . However, in 2,4,6-tribromobenzal bromide ΔS^{\dagger} is zero within experimental error (3) and one may assume a similar value for 2,6-dichlorobenzal iodide.

(c) Comparison with Potential Energy Calculations

The method of calculation (6) allows the deformation of the bond angles indicated in **13**, the stretching of the C—C_{α} bond, and for the nonbonded interactions via a 6–12 potential. The results² are given in Table 3. The calculated barrier of 21.7 kcal/mol is 3% higher than the observed value of 21.0₅ ± 0.1₀ kcal/mol.

When $\omega = 60^\circ$, a C—I bond eclipses a C—Cl bond (see **6**) and the potential energy relative to the ground state is then 76% of the transition state energy at $\omega = 90^\circ$ (see 7). When $\omega = 30^\circ$, one C—I bond lies in a plane perpendicular to the aromatic ring and the energy is 34% of the transition energy. To zero order the energy of the transition state for a CH₂I group should then be 55% of that for a CH₂ group, when both are flanked by C—Cl bonds on the ring. Thus the barrier for a CH₂I group may lie near 21.0 × 0.55 = 11.5 kcal/mol, while for CH₂Cl it may be near 15.3 × 0.55 = 8.4 kcal/mol (3). These

 2 Details of the calculations are available from the authors.

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2		Bond angles (deg)							
ω (deg) $l_{C_1-C_{\alpha}}$	$l_{C_1-C_{\alpha}}$	α	β	γ	E_{nb}	E_1	$E_{\mathbf{ heta}}$	Ε	$E_{\rm rel}$
0	1.510	124	125	113	-1.00	0.08	1.57	0.65	0.00
30	1.525	122	131	118	1.48	0.31	6.16	7.95	7.30
60	1 545	124	135	121	4.58	0.84	11.85	17.28	16.62
90	1.560	133	133	121	6.79	1.41	14.15	22.35	21.70

TABLE 3. Conformational energy calculations for 2,6-dichlorobenzal iodide.*

*Definitions of symbols used: $I_{C_1-C_{\alpha}}$ = bond length C_1-C_{α} in Å; E_{nb} = sum of nonbonded interactions; E_1 = energy for deformation of C_1-C_{α} bond; E_{θ} = sum of bond bending energies; $E = E_{nb} + E_1 + E_{\theta}$ in kcal/mol; $\omega = 0^{\circ}$ when the C_{α} -H bond lies in plane of aromatic ring. Further definitions are given in the explanation of structure 13 in the text.

values are high enough for extraction by a lineshape analysis and are the subject of the next section.

Barriers to Rotation in $m-C_6Cl_4 (CH_2X)_2$ (X = Cl, Br, I)

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(a) Spectral Characteristics and Assignments

In principle, **11** and **12** each possess ABB'A', *i.e.* [AB]₂ resonance spectra (13). Their appearance will be dominated by the large ${}^{2}J_{AB}$ coupling within a methylene group because the coupling between protons in different groups is at least ten times smaller than ${}^{2}J_{AB}$ (14, 15).

In the event, at low enough temperatures the spectrum of each compound displays an AB quartet and, superimposed on the low-field tall peak of this quartet, there occurs a peak of relatively low intensity. The linewidths are about 1 Hz, suggesting the presence of unresolved long-range coupling between protons in different methylene groups. The quartet with a relatively large internal shift may be assigned to one conformer, **11** or **12**, and the single peak must then represent a tightly coupled AB quartet from the other, less abundant, conformer. A probable assignment can be made as follows.

Electric fields (16, 17) from the bond dipoles in 11 and 12 can cause relative chemical shifts of the methylene protons of less than 0.01 p.p.m. A detailed consideration of molecular sizes and packing, and of aromatic solvent induced shifts (18) suggests that the magnetic anisotropy of the toluene- d_8 solvent molecules causes the internal chemical shifts in 11 and 12 and that H_B in the cis form experiences a net shift to high field. Such considerations are consistent with the observation of no internal chemical shift in 8 at considerably lower temperatures than those needed for spectral coalescence in 11. Intramolecular electric fields are again insufficient as causes of internal shifts in 8 and the barrier to rotation will be almost identical in the meta and para isomers,

buttressing effects being rather small in even more crowded compounds (5, 19, 20).

The above interpretation of the observed shifts implies the higher stability of the *cis* form, **11**, at the temperatures in Table 4. Intramolecular electric fields or nonbonded interactions (17) are not large enough to reproduce the ΔG^0 values in Table 4 but the more polar form, **11**, is stabilized by the aromatic solvent by as much as 0.5 kcal/ mol (21–26). The ΔG^0 values in Table 4 are then expected and observed to increase in the order Cl>Br>I. The *cis* form, **11**, is then more stable than the *trans* form, **12**.

(b) Extraction of Rate Constants and Rotational Barriers

The chemical shifts and proton-proton coupling constants of the methylene protons are given in Table 4. The latter are no doubt negative and their magnitudes have the same relative order as those in the corresponding methyl halides (27) and in some benzyl halide derivatives (28). The relative stabilities are presented as ΔG^0 values, obtained by simulation of the welldefined quartet and subtraction of this area from the total area of the observed spectrum.

The exchange process occurs between c, t, c', and t' (Scheme 1) and the spectral types of each form are indicated as ABB'A' etc. The complexity of the process and the moderate quality of the spectra dictated an approximate treatment of the data, yielding ΔG^{\pm} at the coalescence temperature of the well-defined quartet. The exchange broadened spectra were simulated with the program ABXFIT (29) and the fitting method gave the rate of interconversion of c and c'. At equilibrium one has $p_c k_{ct} = p_t k_{tc} = p_c k_{ct'} =$ $k' = p_i k_{tc'}$, etc. The sum of the fractional populations, p, is unity and therefore the rate of the AB exchange is

 $k_{AB} = p_c k_{ct} + p_t k_{tc'} + p_c k_{ct'} + p_t k_{t'c'} = 4k'$

	Value				
Parameter	Cl (°K)	Br (°K)	I (°K)		
V _B *	378.9 (161)	372.7 (196)	368.3 (226)		
$\bar{v_A}$	390.7	383.9	379.1		
v	382.3	375.9	371.4		
$ J_{AB} $ (Hz)	11.8 ± 0.5	11.2 ± 0.2	10.1 ± 0.2		
$G_t^{o} - G_c^{o}$ (kcal/mol)	$1.260 \pm 0.100 (185)$	0.845 ± 0.015 (215)	0.680 ± 0.080 (240)		
$k_{ct} (s^{-1})^{\dagger}$	11.6 ± 5.9 (185)	$11.5 \pm 2.9 (215)$	$12.5 \pm 3(240)$		
$k_{ic} (s^{-1})$	375 ± 125	82.5 ± 21	52 ± 13		
ΔG_{ct}^{\dagger} (kcal/mol)	9.5 ± 0.2	11.1 ± 0.1	12.4 ± 0.1		
ΔG_{tc}^{\dagger} (kcal/mol)	8.2 ± 0.2	10.3 ± 0.1	11.7 ± 0.1		

TABLE 4.	Spectral parameters, relative populations, and rate data for
	α, α' -dihalo-2,4,5,6-tetrachloro- <i>m</i> -xylenes

*Shift in Hz at 100 MHz to low field of internal TMS, temperature in brackets; the center of the resonance of the less abundant isomer is given as v. †The subscripts *ct* refer to the *cis* and *trans* isomers, 11 and 12, of these compounds; see also Scheme 1.



Noting that, for example, k_{ct} is the rate constant for the conversion of c to t, the rate constants and ΔG^{\dagger} values in Table 4 can be deduced.

Generous errors of 25 to 33% in the rate constants and of $\pm 2 \degree C$ in the temperatures were treated by Binsch's method (12) to obtain the quoted errors in ΔG^{\dagger} . For the reasons given above, the ΔG^0 values will likely decrease as the temperature increases, so that ΔG_{ct}^{\dagger} and ΔG_{tc}^{\dagger} will likely converge at higher temperatures.

(c) Comparison of Benzal and m-Xylyl Halide Barriers.

The mean ΔG^{\dagger} values for the *m*-xylyl halides amount to 60% of ΔG^{\pm} values for the corresponding benzal halides (3). Thus, ΔG^{\dagger} in 2,6dichlorobenzal iodide is 21.05 kcal/mol and $(\Delta G_{ct}^{*} + \Delta G_{tc}^{*})/2$ is 12.0₅ kcal/mol in α, α' diiodo-2,4,5,6-tetrachloro-*m*-xylene. The ΔG^{\pm} values are measured at widely different temperatures for the various compounds (3) and we take the constant ratio of 60% for X = Cl, Br, I as a strong indication of very small ΔS^{\pm} magnitudes in the hindered internal rotations. Therefore the potential energy calculations can be equated to ΔG^{\dagger} values with some confidence.

In our opinion these results are evidence for the conformation, 3 or 7, of the activated rotational state of the benzal halides.

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