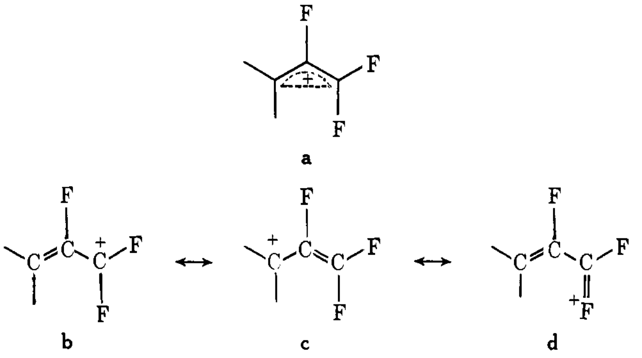
expected to reduce the need for 1–3 π bonding. As the number of terminal fluorines is increased from two (**10**) to three (**12**) to four (**14**) the 1–3 π-bond orders steadily decrease from 0.333 to 0.316 to 0.284, respectively, while the introduction of a fluorine at C_2 causes an increase in this order. Extrapolating these results to the unsubstituted allylic cation, we estimate a π-bond order greater than 0.35. These results indicate hybrid **15a** is not unreasonable to invoke as part of an overall description of ions **10–14**.



15

Examination of the σ- and π-charge densities for ions **10–14** reveals that the addition of fluorine at C_2 places a stronger electron demand at C_1 through its strong negative inductive effect (σ polarization). This −I effect is not counterbalanced by strong π back donation from fluorine to carbon. This is evident in ion **11** where the C_1–F_1 and C_1–F_2 π-bond orders (0.4735 and 0.4607) are far larger than the C_2–F_3 π-bond order of only 0.1829. This qualitatively agrees with a simple valence bond picture where it is impossible to write a resonance hybrid structure with a double bond between C_2 and F_3 without introducing additional charge separation.

It is interesting to note that the total excess negative charge density on F_1 and F_2 decreases going from **10** to **11** and then increases very slightly going from **11** to **12–14**. The addition of fluorine at C_2 inductively polarizes the σ system causing a net drain on charge at F_1 and F_2. In ion **10** where a somewhat larger π back donation from F_1 and F_2 to C_1 occurs than in **12**, **13**, and **14**, these two fluorines also have the greatest excess negative charge density. In other words, here is an example where the negative charge density increases at fluorine despite the fact these fluorines delocalize more positive charge toward carbon by back π donation. This donation is more than compensated by σ polarization from carbon to fluorine.

Acknowledgments. Mr. C. H. Copeland is thanked for valuable assistance in the computer programming problems. Extensive computer time was provided by the University of Alabama Computer Center. In addition, the University of Alabama Research Grants Committee is thanked for financial assistance provided by grant project No. 762.

Acidities of Polyfluorinated Hydrocarbons. II. Hexafluoropropanes, Trifluoroethanes, and Haloforms. Intermediate Carbanion Stability and Geometry

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Abstract: Pseudo-first-order kinetic acidities have been determined for a series of 2-substituted 1,1,1,3,3,3-hexafluoropropanes, 1,1,1-trifluoroethanes, and haloforms by hydrogen, deuterium, and tritium isotope exchange reactions. Techniques of ^{19}F nmr, ir, and scintillation counting were used to determine these acidities. The solvent–catalyst system employed was a 50:50 mol % solution of dimethyl sulfoxide and methanol with triethylamine as catalyst. Internal return and α- and β-halogen elimination reactions of the intermediate carbanions were negligible in this solvent system. The acidity data obtained were interpreted in terms of the stabilities and geometries of the intermediate carbanions involved. In these studies, the two main factors that determine fluorocarbanion and halocarbanion stabilities appear to be induction and destabilization by a +R–p-orbital electron feedback mechanism. Probes of carbanion geometries have been made by consideration of (a) stability trends in the series of anions studied and (b) the fact that the +R destabilization mechanism is most effective in planar structures. The data indicate steric factors and the +R effect have substantial influence on carbanion geometries. Also, it is postulated that although the carbanions studied are either close to planar (sp^2 hybridized) or close to pyramidal (sp^3 hybridized), slight forced changes in the geometry of a carbanion which belongs to either group have a significant effect on the stability of that carbanion.

Carbanions (the conjugate bases of "carbon acids") are common in fluoro and halo organic chemistry in general, since the halogens can stabilize carbanions readily by several effective mechanisms. However, the correct interpretation of the stabilization is difficult since so many rationales have been presented.[2,3]

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(1) NSF Trainee 1965–1968, and Phillips Petroleum Fellow 1968–1969. The majority of this work was taken from the Ph.D. thesis of K. J. K., 1969.

(2) For an excellent review see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, London, 1965.

(3) K. J. Klabunde and D. J. Burton, *J. Amer. Chem. Soc.*, **94**, 820 (1972).

Table I. Kinetic Acidity Data for Isotope Exchange of 2-Substituted 1,1,1,3,3,3-Hexafluoropropanes, 1,1,1-Trifluoroethanes, and Haloforms

Expt	Carbon acid	Temp, °C	Concn, m		Relative[a] rate	pK_a estimate	Probable[m] geometry of conjugate base
			Carbon acid	Triethylamine			
1	$CF_3CH(C_6H_5)CF_3$[b]	37.0	0.86	0.079	1.00 ± 0.02	17.9	Pyramidal[n]
2	CF_3CHFCF_3[c]	37.0	0.93	0.080	0.86 ± 0.03	18.0[o]	Pyramidal
3	$CF_3CHClCF_3$	−14.3	0.89	0.079	17.3 ± 0.5		
4		37.0			651[d] ± 26	12.6	Pyramidal
5	$CF_3CHBrCF_3$[e]	−34.3	0.86	0.079	10.0 ± 0.8		
6		−23.7	0.86	0.079	30.9 ± 2.0		
7		−14.3	0.86	0.079	59.0 ± 7.2		
8		−6.5	0.86	0.079	159 ± 23		
9		37.0			2227[d] ± 290	11.5	Pyramidal
10	CF_3CHICF_3	−14.3	0.86	0.080	4.10 ± 0.16		
11		37.0			154[d] ± 10	13.7	Planar
12	$CF_3CH(OCH_3)CF_3$	56	Too weakly acidic[f]			>22	Pyramidal
13	$(CF_3)_3CH$	−45	0.85	0.013	[g]	11.0[o]	Planar
14	CF_3CF_2H					27[h]	Pyramidal
15	CF_3CCl_2H	37.0	0.85	0.077	2.33 ± 0.10	17.2	Pyramidal
16	CF_3CBr_2H	37.0	0.85	0.078	3.03 ± 0.20	16.9	Pyramidal
17		66.5	0.86	0.078	47.4 ± 1.8	16.6	
18	CF_3CI_2H					17.1[i]	
19	CF_3H					28[o]	Pyramidal
20	CCl_3H[j]	37.0	0.87	0.087	18.2 ± 0.5	15.5	Pyramidal
21	CBr_3H[k]	37.0	0.91	0.088	160 ± 7	13.7	Pyramidal
22	CI_3H					13.7[l]	Pyramidal

[a] Each value is an average of two–four determinations. The errors shown are calculated probable errors. [b] A complete study of this compound has been made.[3] [c] A control experiment employing ^{19}F nmr and an internal standard proved that a correction of the initial concentration (C_0) in solution due to vaporization of the carbon acid at 37.0° was unnecessary. [d] Calculated by the Arrhenius equation[7] and thermodynamic parameters taken from experiments 5–8. [e] Thermodynamic computations yielded[7,8] energy of activation (E_a) = 13.5 kcal/mol; entropy of activation ($\Delta S^{\mp}$) = −20.0 eu. [f] After 96 hr no isotope exchange had occurred. [g] Too reactive for an accurate analysis. A value of 4290 at 37.0° was calculated from relative rate data of Andreades[6] and experiment 2. [h] Estimated from the pK_a of $CF_3(CF_2)_5$-CF_2H.[2,6] [i] Estimated from the data of Hine and coworkers[9] and experiment 16. [j] Actually, k_D was determined for economic reasons, and k_H was calculated employing the observed isotope effect for $CHBr_3$ (2.3). [k] Rates of hydrogen–deuterium, deuterium–hydrogen, and tritium–hydrogen conversions were determined: $k_H/k_D = 2.3$, $k_D/k_T = 1.6$ (calcd $k_H/k_D = 2.9$).[3] [l] Estimated from the data of Hine and coworkers[5b] and experiment 21. [m] These geometries were rationalized from kinetic acidity data in solution. No solid-state crystal studies have been carried out. It is considered that these carbanions need not be "pure" sp^2 or sp^3 hybrids, but should approach one or the other of these pure hybrids. [n] Reference 3. [o] References 2 and 6.

These rationales include fluorine hyperconjugation, induction, polarizabilities, etc.[2,3] In addition, destabilization mechanisms have recently been shown to be important,[3,4] and should be clarified. Streitwieser and Mares[4c] have pointed out that the geometry of the intermediate carbanions have substantial effects on their stabilities, which adds to the complexity. We considered that there have been no comprehensive studies of the effects of various substituents on the stabilities and geometries of fluoro and halo carbanions. In an attempt to elucidate more clearly some of the properties of these carbanions we have carried out kinetic acidity studies of a series of halogenated carbon acids. The acidities of these substrates should be directly proportional to the stabilities of their conjugate bases (carbanions). The carbon acids studied by base-catalyzed hydrogen, deuterium, and tritium isotope exchange are listed (I–III).

CF_3CHXCF_3 I	CF_3CX_2H II	CHX_3 III
X = (a) C_6H_5	(a) Cl	(a) Cl
(b) F	(b) Br	(b) Br
(c) Cl		
(d) Br		
(e) I		
(f) OCH_3		
(g) CF_3		

Method and Results

The advantages of the 50:50 mol % dimethyl sulfoxide (DMSO)–methanol (or DMSO-d_6–methanol-*O-d*) solvent system employed for these kinetic studies have been described.[3] Triethylamine was used as catalyst. It should be emphasized that this solvent–catalyst system allowed kinetic studies without complications of β-fluoride ion eliminations, α-halogen eliminations, and solvent isotope effects.[3] Also, the exchange reactions were first order in substrate and catalyst, and "internal return" was not considered important. The experimental techniques, methods of analyses, and calculations have also been described.[3] For systems I and II, hydrogen–deuterium and deuterium–hydrogen exchange rates were determined by ^{19}F nmr. Tritium–hydrogen conversions were followed by liquid scintillation counting of each isolated sample.[3] Haloform (III) isotope exchanges were followed by ir techniques that have been described by Hine and coworkers.[5]

Table I summarizes the kinetic data obtained. The pK_a estimations (which are crude but useful on a relative basis) were made employing carbon acids Ia, Ib, and Ig as standards.[3,6] For the sake of completeness some

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(4) (a) H. G. Adolph and M. K. Kamlet, *J. Amer. Chem. Soc.*, **88**, 4761 (1966); (b) J. Hine, L. G. Mahone, and C. L. Liotta, *ibid.*, **89**, 5911 (1967); (c) A. Streitwieser, Jr., and F. Mares, *ibid.*, **90**, 2444 (1968).

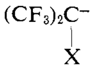
(5) (a) J. Hine, R. C. Peek, and B. D. Oakes, *ibid.*, **76**, 827 (1954); (b) J. Hine, R. W. Burske, M. Hine, and P. B. Langford, *ibid.*, **79**, 1406 (1957).

(6) S. Andreades, *ibid.*, **86**, 2003 (1964).

carbon acids are included in Table I[7-9] that were not analyzed in this study. Their pK_a estimates are made from comparisons of our kinetic data and pK_a determinations with kinetic data obtained by others.

Discussion

Solvent effects, isotope effects, solvent isotope effects, and the exact mechanism of exchange have been discussed for the solvent–catalyst system employed, and will not be presented here.[3] However, the intermediate carbanions in these exchange reactions will be discussed in detail. Since so many mechanisms of halocarbanion stabilization have been postulated (at least ten),[2,5,10] it is important to separate and clarify which of these mechanisms are most important. The halocarbanions which result from carbon acids I, II, and III are shown (IV, V, and VI, respectively). The effects of "X" on the stability and geometry of these carbanions should be maximized since these substituents are bonded directly to the carbanionic carbon atom. Thus, in this close proximity the effects of induction, polarizability, and d-orbital participation should be very significant. Steric factors should also be important. And, lastly, the mechanism of carbanion destabilization by X should be of maximum effectiveness. This destabilization factor (+R effect) has been discussed previously[3] and probably occurs through a p-orbital electron feedback mechanism. A physical picture of this feedback by X to destabilize the transition state for exchange is shown in structure VII (B is the base catalyst).



$(CF_3)_2C^-$–X

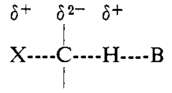
IV

X_2C^-–CF_3

V

X_3C^-

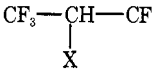
VI



$\overset{\delta+}{X}$----$\overset{\delta 2-}{C}$----$\overset{\delta+}{H}$----B

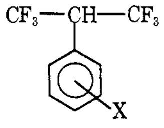
VII

Since partial double bond formation favors destabilization, a planar or sp^2-hybridized transition state would be most susceptible to destabilization. (This argument has been expressed in alternative terms by Hine.)[4b] The data indicate that carbanion IV is stabilized in the order X = CF_3 > Br > Cl > I > C_6H_5 > F > OCH_3. Induction must be quite important, which is shown by comparison of carbon acids I and VIII. When X is insulated from the carbanionic site by a phenyl group the carbon acid acidities are most often substantially lower.[3] Thus, decreasing the inductive stabilization is not compensated for by the opportunity to conjugate with the phenyl ring. The best examples are with X = Cl and Br. In these cases I had much higher acidity than VIII,[3] and the comparisons are valid since the carbanions resulting from these carbon acids are all of the same geometry (pyramidal, *cf.* following discussion).



CF_3–CH(X)–CF_3

I



VIII

Polarization does not appear to be a dominate factor in the stabilization of these carbanions. For the halogen substituents in carbanion IV, this type of stabilization would predict stabilities in the order X = I > Br > Cl > F,[5b] which is not the observed order. The observed order for system IV is X = Br > Cl > I > F. In addition, polarization is of minor importance in p-halogen-substituted carbon acids of structure VIII.[3] Similarly d-orbital effects or "d-orbital participation,"[5b] which stabilizes carbanions by charge dispersion through expansion of the halogen's outer shell to ten electrons, was shown to be of minor importance.[3] Therefore, d-orbital effects are probably not important in system IV either.

Due to the above considerations, we maintain that although many minor effects are probably operative in the stabilization of these carbanions, the observed stabilization order (and thus, orders of acidity) is best explained in terms of only two mechanisms; these are induction and +R destabilization. Following discussion will attempt to further verify this postulate. First of all, it should be noted that the observed order of stabilization by X in system I is not predicted by inductive effects alone, even though previous discussion indicated induction is important. Inductively, the predicted order for the whole series of I is X = F ≈ CF_3 > Cl > Br > I > OCH_3.[5,10,11] Consideration of the +R effect as dominating leads to the predicted order X = CF_3 > I > Br > Cl > F > OCH_3 since the ability of a substituent to "backbond" is in the opposite order.[3] (Perfluoroalkyl groups only stabilize through a strong inductive effect, and have comparatively little ability for +R destabilization.) The predicted order of stabilization from +R considerations is identical with the observed order except for the substituent X = I (iodine). Apparently other factors are important in this case, as discussed later. Additional evidence for a strong +R effect is found in a comparison of the acidities of the four carbon acids Ia, Ib, IX, and X. The inductive effect of the α-fluorine in Ib should overwhelm that of the m- or p-fluorine in IX and X. However, the acidities of Ia, Ib, and X are all about the same (actually Ib is the weakest acid of all four).[3] In Ib and X the +R effect is operable. However, in IX the +R effect for the fluorine atom should not be substantial, and correspondingly, the acidity of IX is 10 times that of the other three. The conclusion that results is that the +R effect of the α-fluorine in Ib overwhelms the inductive effect of the same fluorine. In this regard, the +R destabilization effect can be used to rationalize the data of Andreades,[6] where the acidity of Ig was found to be 1 × 10^9 times greater, and Ib 2 × 10^5 times greater than fluoroform. Fluorine hyperconjugation is not a necessary rationale, since the α-fluorine atoms in fluoroform could *destabilize* the

$C_6H_5CH(CF_3)_2$	Ia	1.00 rel rate
$FCH(CF_3)_2$	Ib	0.86
m-$FC_6H_4CH(CF_3)_2$	IX	18.4
p-$FC_6H_4CH(CF_3)_2$	X	1.57

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(7) K. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill, New York, N. Y., 1965.

(8) K. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964.

(9) J. Hine, R. Wisebock, and R. G. Ghirardelli, *J. Amer. Chem. Soc.*, **83**, 1219 (1961).

(10) K. J. Klabunde, Ph.D. Thesis, University of Iowa, 1969.

(11) W. A. Sheppard, *J. Amer. Chem. Soc.*, **85**, 1314 (1963).

Table II. Physical Properties of Carbon Acids

Carbon acid	Bp, °C	$n^{20}\mathrm{D}$	^{1}H nmr	^{19}F nmr
CF_3CHFCF_3	-12^a		*a*	*a*
$CF_3CHClCF_3$	16^b		4.47 (septet, 1 H) J_{CF_3-H} = 5.75 cps	71.15 (doublet, 6 F)
$CF_3CHBrCF_3$	32	1.3023	4.43 (septet, 1 H) J_{CF_3-H} = 6.26 cps	68.75 (doublet, 6 F)
CF_3CHICF_3	54	1.3528	4.66 (septet, 1 H) J_{CF_3-H} = 7.00 cps	65.37 (doublet, 6 F)
$CF_3CH(OCH_3)CF_3$	50	1.290	3.86 (septet, 1 H) J_{CF_3-H} = 6.31 cps 3.67 (singlet, 3 H)	74.79 (doublet, 6 F)
$(CF_3)_3CH$	18		*a*	*a*

[a] Reference 6. [b] Reference 17.

transition state for exchange by the +R effect much more than trifluoromethyl groups.

The paper by Hine and coworkers on the acidities of the haloforms[5b] in conjunction with Andreades work[6] indicates that the stabilization order in carbanion IV should be X = CF_3 > I > Br > Cl > F > OCH_3.[4b] As mentioned before, the concept of +R destabilization predicts the same order. The substituent X = I is the only one out of the +R predicted order in the present study. The following discussion attempts to rationalize this observation in terms of carbanion geometry, induction, and the +R effect. In addition, the same rationale will be used to explain other abnormalities in the data listed in Table II, such as the unusual trends in acidity in passing from series I to II and to III.

Streitwieser and Mares[4c] have effectively shown that +R destabilization is most effective in planar sp^2-hybridized carbanions. A fluorine atom can reduce carbon acid acidity by many factors of 10 if the intermediate anion is planar as opposed to pyramidal. In fact, a carbon acid that yields a planar carbanion as its conjugate base and that bears an α-fluorine atom is less acidic than the same carbon acid that bears an α hydrogen in place of the fluorine.[4c] Thus, fluorine is capable of a +R effect that more than compensates for its inductive effect compared with hydrogen. Destabilization by the +R effect pictured by structure VII is extremely more effective when VII is planar. This large difference in effectiveness is due to the fact that the electronic charge feedback must occur through the p_z orbital of the substituent X.

In the absence of outside effects such as conjugational substituents and steric strain, carbanions prefer pyramidal geometry. This preference is due to the "s-character effect" which simply depends on the fact that anions are better stabilized if the free pair of electrons has a large probability of being in an orbital richest in s character and, thus, closest to the nucleus.[2] A pyramidal carbanion would have an sp^3 orbital rich in free electron pair density, while in a planar anion it would be a pure p orbital. However, the s-character effect is overwhelmed if strongly conjugational substituents are present, since conjugational stabilization is more effective in a planar structure.[2,4c] Furthermore, the s-character effect may not even be as important as the +R effect in helping a carbanion maintain its pyramidal configuration.[4c] Although little is known about the steric strain factors in the determination of a carbanion's geometry this strain would favor formation of planar anions.[12a] (It should be emphasized at this point that these carbanions need not exist as "pure" sp^3- or sp^2-hybridized species, but may be mixtures of the two. However, the true species should approach sp^3 or sp^2 hybridization, and carbanions probably do not exist as "half" sp^2 and sp^3 since this should be the highest energy point on a potential energy plot. For example, X-ray studies have shown that the effectively conjugated tricyanomethide ion is very *nearly* planar and trigonal in the solid state; ammonium ion was the cation.)[12b]

The probable geometry of carbanion IV where X = C_6H_5 has been deduced as near pyramidal.[3] As X is changed from F to Cl to Br to I to OCH_3 to CF_3 steric strain factors as well as +R effectiveness must also change, and perhaps geometries also change. The data show that the acidities of Ia and Ib are nearly identical. Obviously Ia must be considerably more acidic than the unsubstituted parent compound XI shown below (compare toluene and methane of pK_a 37 and *ca.* 48, respectively).[2] It follows that Ib must also be considerably more acidic than XI. According to the theory of

$CF_3CH(C_6H_5)CF_3$	$CF_3CH_2CF_3$	CF_3CHFCF_3
Ia	XI	Ib

Streitwieser and Mares[4c] discussed before, if a carbon acid is acidified by the replacement of an α hydrogen with an α fluorine, then the intermediate carbanion must be pyramidal. Thus, carbanion IV where X = F is probably pyramidal.

The acidities of Ib, Ic, and Id are in the correct order that would be predicted from the work of Hine and coworkers on the acidities of the haloforms.[5b] The haloform acidities were rationalized in terms of polarizability, d-orbital participation, etc. However, recent work by Adolph,[4a] Hine,[4b] Streitwieser,[4c] and this study[3] have demonstrated the capabilities of fluorine for extremely strong +R destabilization effects. Chlorine, bromine, and iodine are also capable of this effect, only to decreasing extent.[3] It seems reasonable, then, to rationalize the acidities of Ib, Ic, and Id in terms of decreasing +R effectiveness. The acidities are in the correct order of Id > Ic > Ib. In addition, the haloform acidities[5b] might also be rationalized in this manner instead of polarizability and d-orbital participation. Also, since Hine and coworkers[4b] have reported that trihalomethyl anions are most likely pyramidal, and since the acidity order for Ib, Ic, and

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(12) (a) C. Bugg, R. Desiderato, and R. L. Sass, *J. Amer. Chem. Soc.*, **86**, 3157 (1964). (b) A referee has pointed out, however, that comparison of solution *vs.* solid phase preferred carbanion geometries is highly suspect.

Id is the same as the order for the haloforms (X = Br > Cl > F), there is no reason to suspect that IV where X = Cl and Br are not pyramidal also. Thus, we deduce that IV where X = F, Cl, and Br are pyramidal.

In accordance with the rationale that has been presented, the acidity order should be Ie > Id > Ic > Ib (X = I > Br > Cl > F). This order is observed except for Ie (X = I). Perhaps the geometry of the intermediate carbanion (I → IV) can explain this discrepancy. Steric strain factors may force IV where X = I to take on a planar configuration. In the planar case the iodine atom would be more effective at +R destabilization and would lower the acidity of Ie out of the expected range. It could be that steric strain is not great enough in IV where X = F, Cl, or Br to force a planar situation, but is great enough when X = I (the largest substituent). The stabilization gained by relief of strain when X = I may be greater than the added +R destabilization that would result.

An obvious extension of these arguments predicts that the trifluoromethyl carbanion must be a pyramidal species. This idea has already been mentioned by Streitwieser.[4c] Since IV, where X = F, and the trifluoromethyl anion are pyramidal, then it follows that the pentafluoroethyl anion is also pyramidal. For the sake of completeness, it is of interest to deduce the geometry of the tris(trifluoromethyl) carbanion (IV where X = CF_3). In this ion the only force which tends to hold IV in a pyramidal position is the s-character effect. Also, the only force toward planarity is steric strain. Therefore, a determination of the geometry would allow a useful comparison of the two opposing effects.

The van der Waals radii of an iodine atom is 2.15 Å and that of a trifluoromethyl group is calculated as >2.5.[13] Conformational studies of monosubstituted cyclohexanes[14] yield $-\Delta G°$ values (amount of excess energy of the least stable conformer over that of the most stable conformer) of 0.43 kcal/mol for an iodine substituent,[15] and 2.1 kcal/mol for a trifluoromethyl substituent.[16] These considerations indicate that a trifluoromethyl group would create significantly more steric strain in IV than an iodine atom. Since IV where X = I has a probable planar geometry due to steric factors even though additional +R destabilization results, then IV where X = CF_3 should also be planar (and no additional +R destabilization would result).

Since carbanion IV where X = F, Cl, and Br and carbanion VI where X = F, Cl, and Br have been deduced as having probable pyramidal geometries, then carbanion V where X = F, Cl, and Br should also be pyramidal. However, since IV where X = I should be planar while VI where X = I pyramidal, one cannot deduce what geometry V where X = I should have. Table I summarizes the probable deduced geometries.

Acidity trends are of interest in passing from carbon acid system I to II to III. The replacement of one halogen in a haloform (system III) by a trifluoromethyl group (to yield system II) decreases acidities. However, the similar replacement of two halogens (to yield system I) increases the acidities over even that of system III. It is difficult to explain this trend. However, again carbanion geometry lends a possible explanation. Previous considerations indicated that system IV should be the most sterically strained intermediate carbanion (trifluoromethyl groups are larger than halogen atoms). Thus, if X is always the same, passing from system VI to V to IV steric strain should become greater. Perhaps at the same time these pyramidal carbanions deviate more and more from pure sp^3 hybrids. However, in only one case (in carbanion IV where X = I) is there enough strain to force a lapse into a planar configuration. Even slight deviations from pure sp^3 hybridization should allow more effective +R destabilization by the attached halogens. In carbanion V the added +R destabilization by two halogens could more than compensate for added inductive stabilization resulting from the replacement of a halogen by the trifluoromethyl group (from VI to V). However, in IV the added +R destabilization by the single halogen must not be able to even moderately compensate for the added inductive stabilization of two trifluoromethyl groups. Alternatively, the acidity trend may be due to a relatively large deviation of carbanions IV and V from sp^3 hydridization when compared with carbanion VI. Thus, destabilization in V would be large.

In summary, the acidity data in Table I can be rationalized in terms of a delicate balance between only three factors which affect the stabilities of the intermediate carbanions: (a) induction, (b) +R destabilization, and (c) the exact geometries of the intermediate carbanions (which, in turn, affect the importance of +R destabilization). The transition state leading to the carbanion will assume a geometrical configuration that allows a minimum energy in terms of steric strain and electronic stability.

Simplified quantum mechanical calculations would be valuable with some of these anions. Perhaps clarification of the roles of carbanion geometry and +R destabilization would result.

Experimental Section

The instrumentation employed in this work has been described in a previous paper.[3] The ^1H nmr chemical shifts reported are in δ values downfield from the internal standard tetramethylsilane. The ^{19}F nmr chemical shifts are reported in parts per million upfield from the internal standard $CFCl_3$. All nmr spectra were taken as *ca.* 20% solutions in 50–60% deuteriochloroform, 10% tetramethylsilane, and 10% $CFCl_3$. Glpc analyses were carried out with 10 ft × 0.25 in. o.d. analytical columns, and 10 ft × 0.5 in. o.d. preparative columns. The liquid-phase column supports used are listed as follows: 10% Carbowax 20M (A), 20% dinonyl phthalate (B), and 10% fluorosilicone (C). High pressure apparatus and purification of solvents and other chemicals have been described.[3]

Deuteriochloroform and 1,1,1-trifluoro-2,2-dichloroethane (from the Pierce Chemical Co.) were glpc pure, and were used without further purification. Bromoform and 1,1,1-trifluoro-2,2-dibromoethane (Dow Chemical) were purified by washing with aqueous base solution, drying over magnesium sulfate, and then fractional distillation.

2-Bromo-2-hydrohexafluoropropane. A 128-ml Hastelloy C, high-pressure bomb was charged with 50.0 g (0.19 mol) of phosphorus tribromide, followed by the slow addition of 31.0 g (0.19 mol) of bromine. The bomb was cooled in water and 24.8 g (0.15 mol) of 1,1,1,3,3,3-hexafluoro-2-propanol slowly added. The vessel was sealed and heated to *ca.* 300° for 65 hr by means of a small cylindrical heating mantle. After cooling to 0° the bomb was vented and opened, and its contents were washed with 50 ml of ice water followed by 50 ml of a cold dilute sodium hydroxide solution and 50 ml of ice water. The organic layer was analyzed by glpc on

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(13) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithica, N. Y., 1960.

(14) J. A. Hirsch, *Top. Stereochem.*, 1, 199 (1967).

(15) A. J. Berlin and F. R. Jensen, *Chem. Ind.* (*London*), 998 (1960).

(16) E. Della, *Tetrahedron Lett.*, 3347 (1966).

column B which indicated the presence of four main components, the largest one 68% of the total. The mixture was separated by flash distillation followed by preparative phase chromatography. The largest component was isolated in a yield of 3.0 g (8.8%) of product, bp 33°; reported for 2-bromo-2-hydrohexafluoropropane, bp 33.5°.[17] Analysis of the product by glpc, ^{1}H nmr, and ^{19}F nmr showed the absence of any impurities. Also, the ir spectrum of an authentic sample[18] was identical with that of the isolated material.

2-Chloro-2-hydrohexafluoropropane. A 128-ml Hastelloy C, high-pressure bomb was charged with 20.0 g (0.12 mol) of 1,1,1,-3,3,3-hexafluoro-2-propanol followed by slow addition of 41.5 g (0.20 mol) of phosphorus pentachloride. The bomb was sealed and heated to *ca.* 140° for 12 hr and then to *ca.* 290° for 20 hr by means of a small cylindrical heating mantle. The bomb was cooled to *ca.* 100° and vented through a Dry Ice–isopropyl alcohol trap. The volatiles collected in the trap were analyzed by glpc on column B and showed three main peaks. The mixture was separated by preparative phase glpc, the largest component being 2-chloro-2-hydrohexafluoropropane. The yield was 3.0 g (13.5%); reported for 2-chloro-2-hydrohexafluoropropane, bp 16°.[17] Analysis by glpc, ^{1}H nmr, and ^{19}F nmr showed the material was completely pure. Also, the ir spectrum of an authentic sample[19] was identical with that of the product.

2-Hydroheptafluoropropane. This carbon acid was prepared by the method described by Hauptshien (for the *n*-propyl isomer).[20] The yield was 6 g (35%). Analysis by ^{19}F nmr was consistent with reported spectra.[6]

2-Hydro-2-iodohexafluoropropane. The preparation was carried out by the general method of Knunyants.[17,19] The crude product was purified by preparative glpc on column B; reported for 2-hydro-2-iodohexafluoropropane, bp 58°, $n^{20}{}_{D}$ 1.3520.[21]

2-Hydro-2-methoxyhexafluoropropane. The method of Gilbert[21] was used, and purification was carried out by fractional distillation; reported for 2-hydro-2-methoxyhexafluoropropane, bp 50.5°.[21]

Tritiated Deuteriobromoform. This carbon acid was prepared from bromal[22] by the method described by Hine[5b] for the preparation of deuteriobromoform. In this case a mixture of 10 g of deuterium oxide and 0.01 g of tritium oxide in deuterium oxide (1 m-curie/g, obtained from New England Nuclear Corp.) was used.

Tris(trifluoromethyl)methane was obtained from Du Pont Chemical Co.[19]

Kinetic Methods. Procedures used for the preparation and analyses of kinetic samples have been described,[3] and discussed in the text.

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[17] B. L. Dyatkin, E. R. Mochalina, L. T. Lantseva, and I. L. Knunyants, *Chem. Abstr.*, **63**, 14691*a* (1965).

[18] The authors thank Drs. R. E. A. Dear and J. J. Murray of Allied Chemical Co. for a generous authentic sample of 2-bromo-2-hydrohexafluoropropane.

[19] The authors thank Drs. C. B. Krespan and D. C. England of Du Pont Chemical Co. for generous samples of 2-chloro-2-hydrohexafluoropropane, 2-hydrohexafluoroisobutyric acid, and tris(trifluoromethyl)methane.

[20] M. Hauptshien, A. J. Saggiomo, and C. S. Stokes, *J. Amer. Chem. Soc.*, **78**, 680 (1956).

[21] E. E. Gilbert, *Chem. Abstr.*, **68**, 12474z (1968).

[22] "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 87.

Interaction between *p*-Dimethoxybenzene and Norbornylene in Two Rigid Model Compounds[1]

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Abstract: Nonconjugated *p*-dimethoxybenzene (D) and norbornylene (N) have been incorporated in the same molecule at separations of 2.4 and 4 Å in two rigid model molecules, 3′,6′-dimethoxybenzonorbornadiene (**1**) and 5,8-dimethoxy-*endo,exo*-1,4:9,10-dimethano-1,4,6,7,9,10-hexahydroanthracene (**2**), respectively. The interaction between the D and N π chromophores in the two model compounds was studied spectroscopically and photochemically. The uv absorption indicated that the increase in D–N separation takes the chromophores from a rather strong mutual perturbation in **1** to weak interaction in **2**. The fluorescence quantum yields of **1** and **2** were the same and equal to those of their dihydro analogs. This, together with the results of experiments in which the four compounds were used as sensitizers in the cis–trans isomerization of piperylene, showed that the $S_1 \rightsquigarrow T_1$ intersystem crossing within D in **1** or **2** is not affected by the presence of N in close proximity. Model compounds **1** and **2** were found to undergo clean photoisomerizations either under direct D excitation or on intermolecular triplet sensitization with formation of photoproducts in which the norbornylene unsaturation is changed to an alicyclic group. Differences in photochemical quantum yields and structure of respective photoproducts suggest two different mechanisms.

The study of intramolecular interaction between nonconjugated chromophores offers distinct advantages and gives additional information which is not available from binary mixed solutions.[2] Using inflexible model compounds one may gain insight in the behavior of chromophores (or molecules) in close proximity and one may ultimately understand in detail the configuration and properties of molecular ground and excited

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[1] Taken in part from the dissertation of D. S. C. Chang submitted to the Graduate School of The George Washington University in partial fulfillment of the Ph.D. degree, 1970.

[2] (a) O. Schnepp and M. Levy, *J. Amer. Chem. Soc.*, **84**, 172 (1962); (b) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.*, **85**, 2670 (1963); (c) S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, **87**, 995 (1965); (d) R. A. Keller and L. J. Dolby, *ibid.*, **89**, 2768 (1967); (e) *ibid.*, **91**, 1293 (1969); (f) R. D. Rauh, T. R. Evans, and P. A. Leermakers, *ibid.*, **90**, 6897 (1968); (g) D. E. Breen and R. A. Keller, *ibid.*, **90**, 1935 (1968); (h) D. R. Roberts and E. H. White, *ibid.*, **92**, 4861 (1970); (i) D. F. Roswell, V. Paul, and E. H. White, *ibid.*, **92**, 4855 (1970); (j) A. A. Lamola, *ibid.*, **92**, 5045 (1970); (k) R. P. Hangland, J. Yguerabide, and L. Stryer, *Proc. Nat. Acad. Sci. U. S.*, **63**, 23 (1969); (l) H. Morrison, *J. Amer. Chem. Soc.*, **87**, 932 (1965); (m) H. Morrison and R. Peiffer, *ibid.*, **90**, 3428 (1968); (n) H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5968 (1967); (o) P. A. Leermakers, J. Montiller, and R. D. Rauh, *Mol. Photochem.*, **1**, 57 (1969).