

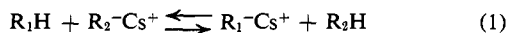
# Acidity of Hydrocarbons. XLIII. Equilibrium Acidity of Some Acidic Hydrocarbons in Cyclohexylamine. Solvent and Ion Pair Effects<sup>1</sup>

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**Abstract:** The  $pK$ 's of a number of relatively acidic hydrocarbons have been determined in the cesium cyclohexylamide-cyclohexylamine solvent system: 1,1,3,3-bis(4,5-phenanthrylene)propene, 13.26; 1,1,3,3-bis(biphenylene)propene, 13.77; 1,3-diphenylindene, 13.92; 1,12-(*o*-phenylene)-7,12-dihydropleiadene, 15.36; 9-phenyl-3,4-benzofluorene, 15.67; bishomofluoradene, 17.26. These  $pK$ 's are relative to 9-phenylfluorene = 18.49. The  $pK$ 's of the first three hydrocarbons and fluoradene were also measured in several other systems: cyclohexylamine without added base, lithium cyclohexylamide-cyclohexylamine, and potassium *tert*-butoxide-dimethyl sulfoxide. Consistencies and differences in the relative acidities in the various solvent systems are explained by electrostatic interactions between cations and carbanions. These interactions are sensitive to the size of the cations, the charge distribution of the carbanions, and the polarity of the solvents.

Recently, considerable attention has been received in the measurements of  $pK$  of acidic hydrocarbons by various methods.<sup>2-7</sup> In our studies of the equilibrium acidities of hydrocarbons in cyclohexylamine (CHA)<sup>2b</sup> a mixture of two hydrocarbons is treated with an insufficient amount of cesium cyclohexylamide (CsCHA) in CHA. This method provides a direct measurement of the difference in acidity of two compounds as expressed in the equilibrium



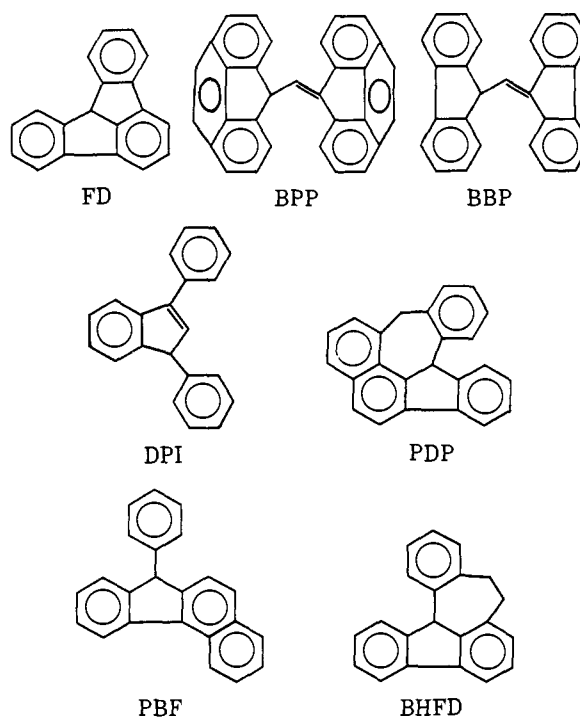
$$K = [R_2H][R_1^-Cs^+]/[R_1H][R_2^-Cs^+] \quad (2)$$

$$\log K = pK(2) - pK(1) \quad (3)$$

This paper reports some new results on  $pK$ 's of hydrocarbons which are more acidic than those we have studied previously. Moreover, we have found that several highly acidic hydrocarbons can ionize in the solvent CHA in the absence of added base to produce colored carbanion solutions. For these compounds we have obtained the "absolute"  $pK$ 's in CHA.

When the  $pK$ 's of 1,1,3,3-bis(4,5-phenanthrylene)propene (BPP), 1,1,3,3-bis(biphenylene)propene (BBP), and fluoradene (FD) in CHA were compared to Kuhn's results<sup>4b</sup> in DMSO, it was found that the relative  $pK$ 's between FD and BPP or BBP changed by more than 1  $pK$  unit between CHA and DMSO, whereas the relative acidity of BPP and BBP remained nearly the same in the two solvent systems. These unexpected

differences prompted a further study of the acidities of BPP, BBP, FD, and 1,3-diphenylindene (DPI) in *tert*-BuOK-DMSO and lithium cyclohexylamide-cyclohexylamine (LiCHA-CHA).



## Experimental Section

Preparations of lithium and cesium cyclohexylamides in cyclohexylamine have been reported previously.<sup>2</sup> Dimethyl sulfoxide was purified by the procedure of Kuhn and Rewicki.<sup>5</sup> This procedure involves partial freezing, vacuum distillation, drying with molecular sieves, and a final vacuum distillation. Highly purified DMSO is also available commercially from Regis Chemical Co. Both solvents were used and gave consistent and satisfactory results. Potassium *tert*-butoxide in dimethyl sulfoxide (*tert*-BuOK-DMSO) was prepared as follows. About 0.1 g of potassium was washed in *tert*-butyl alcohol for 1 min and then allowed to react

(1) This research was supported in part by Grant No. GM-12855 of the National Institutes of Health, U. S. Public Health Service.

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Table I. Carbanion Spectra in Various Solvent Systems

Hydrocarbon	$\lambda_{\text{max}}^{\text{nm}} (\epsilon_{\text{max}})$			
	CHA	CsCHA-CHA	LiCHA-CHA	<i>tert</i> -BuOK-DMSO
FD	365, 378, 546	364, 380, 518 (3,400), 556 (4,200)	522 (3,950), 562 (6,450)	373, 390, 524 (3,790), 564 (4,910)
BPP	553	552	554 (139,000)	557 (135,000)
BBP	554	553	556 (95,200)	559 (105,000)
DPI	382, 432	384 (21,500), 428 (21,850)	376 (22,200), 443 (25,900)	378 (19,400), 445 (23,500)
PDP		392 (14,100), 446 (11,350)		
PBF		382 (19,500), 446 (1,900), 496 (4,500), 528 (4,050)		

<sup>a</sup> Spectral data for BHFD in CsCHA-CHA were published in ref 12.

with 20 ml of *tert*-butyl alcohol under argon at room temperature. The *tert*-butyl alcohol was vacuum transferred and to this purified *tert*-butyl alcohol was added about 0.2 g of potassium (washed in purified *tert*-butyl alcohol) under argon purge at room temperature. After the reaction was complete, the solvent was removed by vacuum transfer and the residue was dried by pumping out the trace amount of residual solvent. The purified DMSO (10 ml) was syringed into the dry solid light yellow *tert*-BuOK, under the argon purge, to form the *tert*-BuOK-DMSO solution.

The hydrocarbons studied are all known compounds. Fluoradene was supplied by Kinsey and Rapoport, mp 130.5–131.5° (lit.<sup>9</sup> mp 129.8–130.3°). 1,12-(*o*-Phenylene)-7,12-dihydropleiadene (PDP) was the gift of Professor Lansbury.<sup>10</sup> 9-Phenyl-3,4-benzofluorene<sup>11</sup> (PBF) and bishomofluoradene<sup>12</sup> (BHFD) were reported previously. 1,1,3,3-Bis(4,5-phenanthrylene)propene was prepared by allowing 4,5-methylenephenanthrene to react with *n*-butyllithium to produce the lithium salt, which was then treated with ethyl formate to give BPP, mp 275–270° (lit.<sup>13</sup> mp 276–277°). 1,1,3,3-Bis(biphenylene)propene was prepared by the same method starting with fluorene, mp 215–216° (lit.<sup>14</sup> mp 205–206°). 1,3-Diphenylindene was prepared by cyclization of  $\beta,\beta$ -diphenylpropionic acid with polyphosphoric acid to yield 3-phenylindanone, which was treated with phenyllithium to produce 1,3-diphenylindan-1-ol. This alcohol was dehydrated by treatment with polyphosphoric acid to yield DPI, mp 69–70° (lit.<sup>15</sup> mp 71–72°).

The apparatus and the procedure for spectral measurements in CHA have been described.<sup>2</sup> For measurements in DMSO, the solvent was injected directly into the apparatus by a syringe instead of by vacuum transfer. In all of the hydrocarbons studied here, the carbanion spectra developed immediately after the base was introduced. The equilibrium between the hydrocarbon(s) and their anion(s) was also established instantly in CHA, CsCHA-CHA, and LiCHA-CHA. However, in DMSO the equilibrium was reached more than 1 hr after addition of the *tert*-BuOK. The spectral results are summarized in Table I. The equilibrium constants measured are summarized in Tables II, III, IV, and V, where

Table II. Equilibrium Constants in CsCHA-CHA

R <sub>1</sub> H	R <sub>2</sub> H	K <sup>a</sup>	n <sup>b</sup>	Log K
BPP <sup>c</sup>	DPI	4.57 ± 0.24	3	0.66 ± 0.2
BBP <sup>c</sup>	DPI	1.44 ± 0.03	2	0.15 ± 0.01
DPI	PDP	27.3 ± 2.9	3	1.44 ± 0.04
DPI	PBF	56 ± 15	3	1.75 ± 0.11
PDP	PBF	2.06 ± 0.14	3	0.31 ± 0.03
PDP	BHFD	80.2 ± 9.9	7	1.90 ± 0.05
PDP	9-PF	1363 ± 156	6	3.13 ± 0.05

<sup>a</sup> K is defined in eq 2. <sup>b</sup> Number of runs. <sup>c</sup>  $\epsilon_{\text{max}}$  of carbanion in DMSO was used.

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Table III. Ionization Constants in CHA

Hydrocarbons	100K <sup>a</sup>	n <sup>b</sup>	–Log K (pK)
FD <sup>c</sup>	36.7 ± 3.3	4	0.44 ± 0.04
BPP <sup>d</sup>	4.15 ± 0.07	2	1.38 ± 0.01
BBP <sup>d</sup>	0.90 ± 0.10	2	2.05 ± 0.05
DPI <sup>e</sup>	0.623 ± 0.029	2	2.21 ± 0.02

<sup>a</sup> K is defined in eq 5. <sup>b</sup> Number of runs. <sup>c</sup>  $\epsilon_{\text{max}}$  of 4500 was used for its anion at 546 nm. <sup>d</sup>  $\epsilon_{\text{max}}$  of carbanion in DMSO was used. <sup>e</sup>  $\epsilon_{\text{max}}$  of 20,000 was used for its anion at 432 nm.

Table IV. Equilibrium Constants in *tert*-BuOK-DMSO

R <sub>1</sub> H	R <sub>2</sub> H	K <sup>a</sup>	n	Log K
BBP	DPI	19.1 ± 3.2	2	1.28 ± 0.06
FD	BBP	1.94 ± 0.17	2	0.92 ± 0.04
BPP	FD	2.36 ± 0.62	2	0.37 ± 0.11

<sup>a</sup> Same expression as in eq 2 except the carbanions are free ions.

Table V. Equilibrium Constants in LiCHA-CHA

R <sub>1</sub> H	R <sub>2</sub> H	K <sup>a</sup>	n	Log K
BBP	DPI	13.3 ± 2.4	2	1.12 ± 0.08
BPP	DPI	51.0	1	1.71

<sup>a</sup> Same expression as in eq 2 except the cation is lithium instead of cesium.

the more acidic hydrocarbon in each pair is listed first.

## Results and Discussion

**Spectral Results.** Spectral data for the carbanions in CHA, CsCHA-CHA, LiCHA-CHA, and *tert*-BuOK-DMSO are summarized in Table I. In CsCHA-CHA, for BBP and BPP at low base concentration, both expected anions were formed as indicated by their  $\lambda_{\text{max}}$  at 553 and 552 nm, compared with 559 and 557 nm, respectively, measured in *tert*-BuOK-DMSO, and their high extinction coefficients ( $\epsilon \sim 10^5$ ).<sup>8</sup> However, at higher base concentrations, both anion spectra were entirely changed to new spectra, and the spectra at lower base concentration could be regenerated, although with reduced intensity, upon addition of a few drops of methanol.

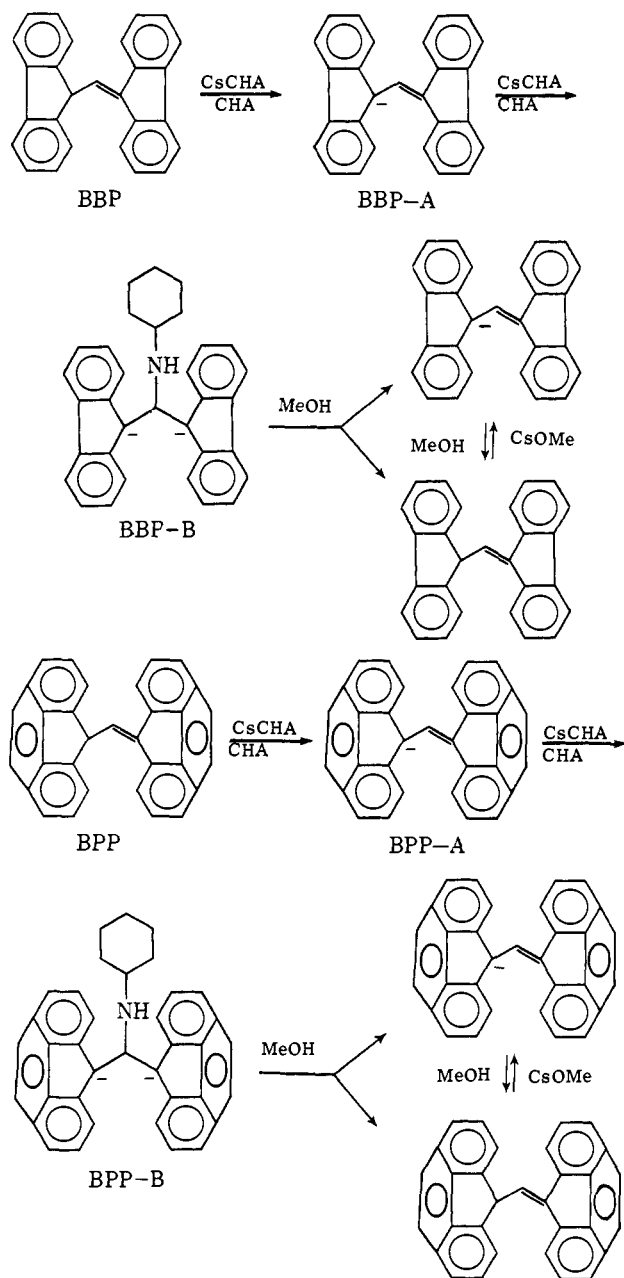
For BBP, the spectrum at higher base concentration was almost identical with the spectrum of 9-alkylfluorenylcesium; that is  $\lambda_{\text{max}}^{\text{nm}} (\epsilon)$  for BBP, 480 (2050), 512 (2280), 546 (1940) compares with 447 (~900), 505 (~1100), 541 (~780) for the latter.<sup>16</sup>

For BPP, the spectrum at higher base concentration,  $\lambda_{\text{max}}^{\text{nm}} (\epsilon)$  540 (10,600), was similar to the spectrum of

(16) A. Streitwieser, Jr., C. J. Chang, and D. M. E. Reuben, *J. Amer. Chem. Soc.*, in press.

4,5-methylenephenanthrylcesium,  $\lambda_{\max}^{nm}(\epsilon)$  505 (6850). In both cases the ratios of the extinction coefficients to the standard are roughly 2:1. These results are consistent with the interpretation in Scheme I which in-

Scheme I



volves the formation of dianions. All of the anions in Scheme I should be ion pairs; the gegenion  $\text{Cs}^+$  is omitted for simplicity. The anions BBP-A and BPP-A are responsible for the spectra at lower base concentration, and the dianions BBP-B and BPP-B, resulting from the addition of CsCHA to double bonds, are responsible for the spectra at higher base concentration. Because of this additional reaction at higher base concentration, it is difficult to obtain good values for the extinction coefficients of BBP-A and BPP-A. Therefore,  $\epsilon_{\max}$  was taken as  $1.12 \times 10^5$  and  $1.41 \times 10^5$  (in *tert*-BuOK–DMSO), respectively, from Kuhn and Rewicki,<sup>8</sup> and were used for the equilibrium acidity measurements. A 20% error in  $\epsilon$  causes less than 0.1 uncertainty in pK. In LiCHA, the anion

spectra of those two hydrocarbons remained unchanged at high base concentration. LiCHA is clearly an effectively weaker base than CsCHA toward these systems so that further addition of the base to the monoanion to form the dianion does not occur.

Based on the results of temperature dependence studies of several carbanion spectra,<sup>17</sup> a plausible hypothesis is that the cesium salts of hydrocarbons studied here are contact ion pairs in CHA, whereas the lithium carbanions are mainly solvent-separated ion pairs in CHA; that is, in the dianions the two fluorenyl anion moieties are undoubtedly twisted with respect to each other and derive substantial stabilization from electrostatic attraction to cesium cations such that the assembly resembles two contact ion pairs bonded together. The spectral results in Table I support this hypothesis. For contact ion pairs, bathochromic shifts in absorption maxima have been shown to occur for a variety of anionic species on increasing the radius of the cation.<sup>18–20</sup> The same phenomenon has also been observed for fluorenyl carbanion.<sup>21</sup> The cause of this shift has been plausibly explained<sup>19,20</sup> as a perturbation of the molecular energy levels by the positive field of the cation. The change in the energy levels should be roughly proportional to the reciprocal of the appropriate interionic separation. In the case of a solvent-separated lithium ion pair, the increase in the effective cationic radius is greater than that of a cesium contact ion pair and accounts for the observed bathochromic shift. For *tert*-BuOK–DMSO in Table I, a further bathochromic shift is observed that undoubtedly corresponds to the greater interionic separation of the solvent-separated ion pair or free ion.

**Acidity Order. Cation and Solvent Effects.** The validity and the experimental error of equilibrium acidity measurements in CsCHA–CHA have been discussed previously.<sup>2</sup> Table II shows the results of these measurements. The replicate experiments often gave agreement to better than  $\pm 10\%$  although in some cases the reproducibility was considerably less. On taking the logarithm, these uncertainties are acceptably small. The direct measurement of DPI relative to PBF gave  $\log K = 1.75$ . The sequence DPI, PDP, PBF gives  $\log K = 1.44 + 0.31 = 1.75$ , the same value as by direct measurement.

Solutions of FD, BPP, BBP, and DPI are colored in CHA, undoubtedly because of ionization to carbanions in this basic solvent. The absorbance is linear in the concentration of hydrocarbon as illustrated by the example in Figure 1; hence, ion pairs are involved as in eq 5 and 6. It can easily be shown that the slope in Figure 1 is proportional to  $K/(1 + K)$ . If dissociated cyclohexylammonium and carbanide ions were involved, a nonlinear dependence on concentration would have resulted. The involvement of ion pairs is supported by the comparison of

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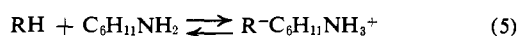
(21) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

Table VI.  $pK$ 's of Hydrocarbons in Various Solvent Systems

Hydrocarbon	Symbol	CsCHA-CHA <sup>a</sup>	CHA <sup>b</sup>	(C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> N-DMSO <sup>c</sup>	<i>tert</i> -BuOK-DMSO <sup>d</sup>	LiCHA-CHA <sup>e</sup>
Fluoradene	FD		0.44 (-0.94) <sup>f</sup>	13.77 (0.34)	13.80 (0.37)	
1,1,3,3-Bis(4,5-phenanthrylene)propene	BPP	13.26 (0.00)	1.38 (0.00)	13.43 (0.00)	13.43 (0.00)	12.21 (0.00)
1,1,3,3-Bis(biphenylene)propene	BBP	13.79 (0.53)	2.05 (0.67)	14.17 (0.74)	14.09 (0.66)	12.80 (0.59)
1,3-Diphenylindene	DPI	13.92 (0.66)	2.21 (0.83)		15.40 (1.97)	13.92 (1.71)
1,12-( <i>o</i> -Phenylene)-7,12-dihydropleiadene	PDP	15.36				
9-Phenyl-3,4-benzfluorene	PBF	15.67				
Bishomofluoradene	BHFD	17.36				

<sup>a</sup> Based on  $pK$  of 9-phenylfluorene = 18.49; see ref 2 (water as standard state). <sup>b</sup> Absolute  $pK$  in CHA (CHA as standard state). <sup>c</sup> Based on  $pK$  of 9-cyanofluorene = 11.40; see ref 4b (water as standard state). <sup>d</sup> Based on  $pK$  of BPP = 13.43, from results in (C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>N-DMSO. <sup>e</sup> Based on  $pK$  of DPI = 13.92, from results in CsCHA-CHA. <sup>f</sup> Number in parentheses is  $pK$  relative to  $pK$  of BPP as 0.00.

spectra in Table I; in fact, the general similarity of the CHA spectra to those of the cesium salts suggests that the cyclohexylammonium carbanide ion pairs involved are of the contact type but that hydrogen bonding with these highly delocalized carbanions must at best be rather weak. Equilibrium constants could be obtained as defined in eq 6 by assuming that the extinction coeffi-



$$K = [R-C_6H_{11}NH_3^+]/[RH] \quad (6)$$

icients of the carbanion salts are the same as the cesium salts. The  $pK$ 's so obtained, as shown in Table III, refer to the solvent CHA as the standard state. The  $pK$ 's (Table VI) measured in CsCHA-CHA are approximately related to water as the standard state.

The relative  $pK$ 's are comparable in CHA and in CsCHA-CHA for DPI, BPP, and BBP as shown in Table VI. This suggests that an extrapolation of our  $pK$ 's as measured in CsCHA-CHA into the absolute  $pK$ 's in CHA should be practical.

The results of the equilibrium constant measurements of FD, BPP, BBP, and DPI in *tert*-BuOK-DMSO are summarized in Table IV. When the results of these four compounds are compared with those in CHA (or CsCHA-CHA) as shown in Table VI, we note that the relative acidity between BPP or BBP and FD or DPI changes by more than 1  $pK$  unit in going from CHA to DMSO, whereas the relative acidity between BPP and BBP, or between FD and DPI, is nearly the same in both solvent systems. The increase in relative acidity of BPP and BBP over that of FD and DPI in going from CHA to DMSO could perhaps be attributed to differences in dispersion interactions<sup>3b,22</sup> of the anions with solvent. Dispersion interactions should be more important for the larger, more delocalized and more polarizable anions of BPP and BBP with the more polarizable solvent DMSO. However, all of these carbanions are large, delocalized, and polarizable and this explanation seems weak and *ad hoc*. A more convincing explanation is based on simple electrostatic interactions between almost free ions in DMSO,<sup>5a</sup> compared with ion pairs in CHA and CsCHA-CHA. Electrostatic attraction between the carbanion and cation in ion pair species is undoubtedly substantial. In the anions from BPP and BBP, the negative charge is delocalized into the two ring systems separated by a

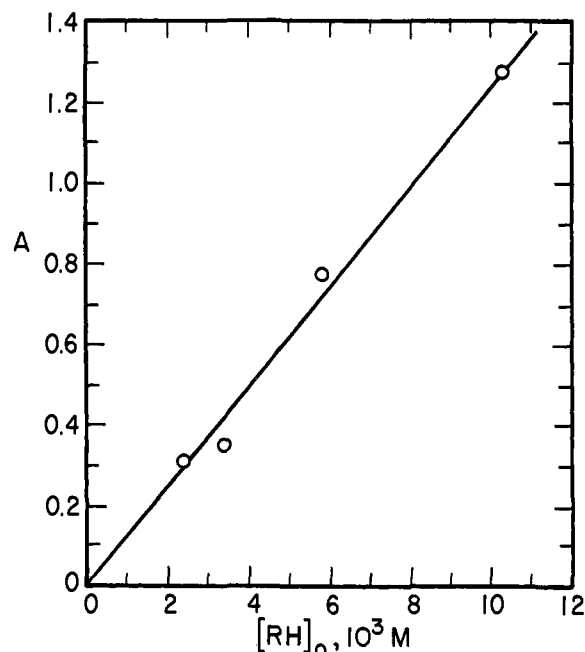


Figure 1. Absorbance of a solution of fluoradene in cyclohexylamine as a function of hydrocarbon concentration.

carbon; that is, these anions have two regions of one-half charge each. The anions from FD and DPI, however, have essentially single regions of a full charge. Accordingly, one would expect that in ion pairs, the anions of BPP and BBP gain less stability than those of FD and DPI from electrostatic interaction with the cation, and results in a decrease in the relative acidities of BPP and BBP in going from DMSO to CHA. If this argument is correct, one would expect that this effect of electrostatic attraction would be less significant in the LiCHA-CHA solvent system in which the anions exist mainly as solvent-separated ion pairs and in which the distance between the charges is greater than in the contact ion pairs. Therefore, we are led to predict that the relative acidity between BPP or BBP, and FD or DPI, in LiCHA-CHA should lie inbetween the other two solvent systems.

The relative  $pK$ 's in LiCHA-CHA were measured for BPP, BBP, and DPI. The results are shown in Table V. Since FD dissociates to give its anion spectrum to a substantial extent in CHA alone, and since there are substantial spectral differences between the ammonium

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salt and lithium or cesium salts, it was not possible to measure directly the  $pK$  of FD in either LiCHA-CHA or CsCHA-CHA.

The results in LiCHA-CHA and other solvent systems are summarized in Table VI. The relative acidity between BPP and BBP, or between FD and DPI, is nearly the same in all of the solvent systems we have studied. For example, FD is more acidic than DPI by 1.77  $pK$  units in CHA, an ion pair system, quite close to the 1.6  $pK$  unit difference in DMSO or for ionic equilibria in  $\text{NaOCH}_3\text{-CH}_3\text{OH}$ .<sup>23</sup>

However, BPP is more acidic than DPI by 0.66  $pK$  unit in CsCHA-CHA, 1.71 units in LiCHA-CHA, and 1.97 units in DMSO; BBP is more acidic than DPI by

(23) A. Streitwieser, Jr., C. J. Chang, and A. T. Young, Jr., *J. Amer. Chem. Soc.*, in press (paper XXXIX).

0.15  $pK$  unit in CsCHA-CHA, 1.12 units in LiCHA-CHA, and 1.31 units in DMSO. The general similarity of the relative  $pK$ 's in CsCHA-CHA and in CHA itself where available further suggests that the cyclohexylammonium carbanide ion pairs involved in CHA are of the contact type. The results for LiCHA-CHA accord completely with the predictions of the electrostatic treatment. This set of results provides further emphasis of the care required in the use of relative acidities when ion pairs are involved; however, it is also clear that changes in relative acidities are frequently understandable from straightforward considerations of solvation and electrostatic interactions. The present results, for example, completely confirm the applicability of simple electrostatic concepts as developed in the preceding paper.<sup>17</sup>

## Ground States of $\sigma$ -Bonded Molecules. XVII.<sup>1</sup> Fluorine Compounds<sup>2</sup>

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**Abstract:** MINDO/2 has been extended to compounds containing carbon, hydrogen, and fluorine, using an improved scheme, based on Oleari's method for the one-center integrals. The calculated heats of formation, molecular geometries, dipole moments, and ionization potentials agree well with experiment. The calculations cover *ca.* 90% of molecules for which reasonably reliable experimental data are available.

Previous papers of this series<sup>1,4,5</sup> have described a semiempirical SCF all-valence-electron MO treatment of ground states of molecules, the parameters being chosen to optimize calculated heats of formation and molecular geometries. The treatment involves two numerical parameters per atom pair; values for these were determined for molecules derived from carbon, hydrogen, nitrogen, and oxygen. Here we describe an extension of MINDO/2 to compounds containing carbon, hydrogen, and fluorine. Parameters for the pairs NF and OF have not yet been determined because there is a dearth of thermochemical data for compounds containing them.

Preliminary attempts to extend MINDO/2 to fluorine were not very satisfactory. We eventually became convinced that these difficulties were consequences of another failing of MINDO/2, its overestimation of dipole moments by *ca.* 50%. The corresponding errors in calculated charge distributions seemed likely to cause peculiar difficulties in compounds containing

fluorine since the charges in them are especially large. We have now found that the calculation of dipole moments can be improved by abandoning the simplifying assumptions previously made in MINDO/2 in the estimation of one-center integrals and these changes did indeed solve the fluorine problem as well. Since the changes do not alter the results of MINDO/2 calculations in any other respect, they seem to represent a worthwhile advance. While only compounds containing C, H, and F are discussed in this paper, parameters are also given for C, H, O, and N.

**Theoretical Procedure.** In the MINDO method,<sup>6</sup> none of the one-center integrals are neglected. There are therefore eight such integrals to be determined for atoms in their valence states, *viz.*

$$U_{ss}, U_{pp}, g_{ss}, g_{sp}, g_{pp}, g_{pp'}, h_{sp}, h_{pp'} \quad (1)$$

where

$$g_{\mu\nu} = (\mu\mu, \nu\nu); h_{\mu\nu} = (\mu\nu, \mu\nu) \quad (2)$$

In MINDO/1<sup>6</sup> and MINDO/2<sup>4</sup> these are determined from the Slater-Condon parameters as follows:

$$g_{ss} = g_{sp} = F^0; g_{pp} = F^0 + 4/25F^2; g_{pp'} = F^0 - 2/25F^2; h_{sp} = 1/3G^1; h_{pp'} = 3/25F^2 \quad (3)$$

The values for  $F^2$  and  $G^1$  were those used also by Pople,

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