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SHORT COMMUNICATION

THE ACIDITY OF FLUORINATED BICYCLOALKANES.

1. 1<u>H</u>-UNDECAFLUORO- AND 1<u>H</u>,4<u>H</u>-DECAFLUOROBICYCLOHEPTANES

IAN W. PARSONS

Chemistry Department, The University of Birmingham, P.O. Box 363,
Birmingham B15 2TT (Great Britain)

SUMMARY

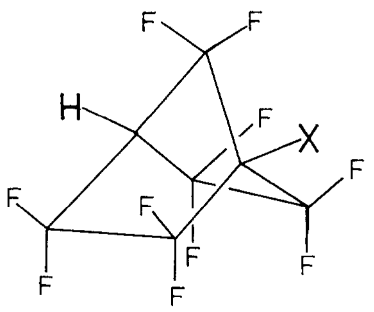
CNDO/2 Calculations have been performed on the title compounds and on the anions derived from them. The results indicate that in the anion there is significant transannular transfer of charge to the 4-position. The amount of such transfer is effectively independent of the 4-substituent. It is concluded that the effect of the substituent upon the stability of the acid must be an important factor.

INTRODUCTION

Ever since the first controlled fluorination of bicyclo[2,2,1] heptadiene [1] over cobalt (III) fluoride showed that substantial amounts of 1 and 2 are isolable from the fluorination mixture, the unusually high acidity of the bridgehead hydrogen atoms in these compounds has attracted the interest of both synthetic and physical organic chemists.

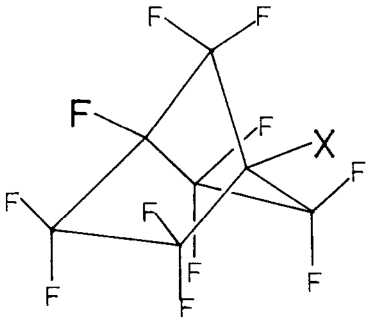
The synthetic uses of the acidity of these materials is well documented, with e.g. the carbanions 1a or 2a showing good properties as a nucleophile and hence giving rise to a range [2] of bridgehead-substituted materials. Further reactions of some of these also give 1,4-disubstituted materials from 1.

More quantitative studies have estimated [3] that the pK_A of 1 (in cyclohexylamine) is 22·3 and that for 2 is 20·5, whilst synthesis [4] of 1<u>H</u>-4-trifluoromethyldecafluorobicyclo[2,2,1]heptane has permitted the measurement of it's pK_A as 20·7 [3].



1 X=H

1a X=⊖



2 X=H

2a X=⊖

The present paper presents the results of a CNDO/2 [5] study of some factors which may be concerned in this acidity. Two main factors may, clearly, operate here: firstly, the heavy fluorine substitution β to the acidic hydrogen must act to stabilise the anionic charge by inductive delocalisation; and secondly there is the possibility of important delocalisation of anionic charge 'through space' from the 1 to the 4 position, possibly using the smaller lobe of the relevant sp^3 hybrid orbital of the anion.

This latter process would lead to a strong dependence of the gas phase acidity and, because of the remoteness of the change in the molecule at C4 from the anionic site at C1 and its probable small effect on solvation, of the liquid phase acidity on the nature of the 4-substituent. The pK_A valves mentioned, and others [3], tend to support this. It is hoped that the present study will shed some light on this.

DETAILS OF CALCULATIONS

Calculations were performed using a modified version of QCPE 91 [6] on the University's ICL 1906A computer. The geometry used is largely an experimental one [7], slightly modified to take account of the difficulty of locating hydrogen atoms in a heavy molecule. The C-H bonds were assumed to be 1·08 A [5] and the bond angles were assumed to be the same for 1$\underline{H}$ as for 1F substitution. The axis system used is shown in figure 1.

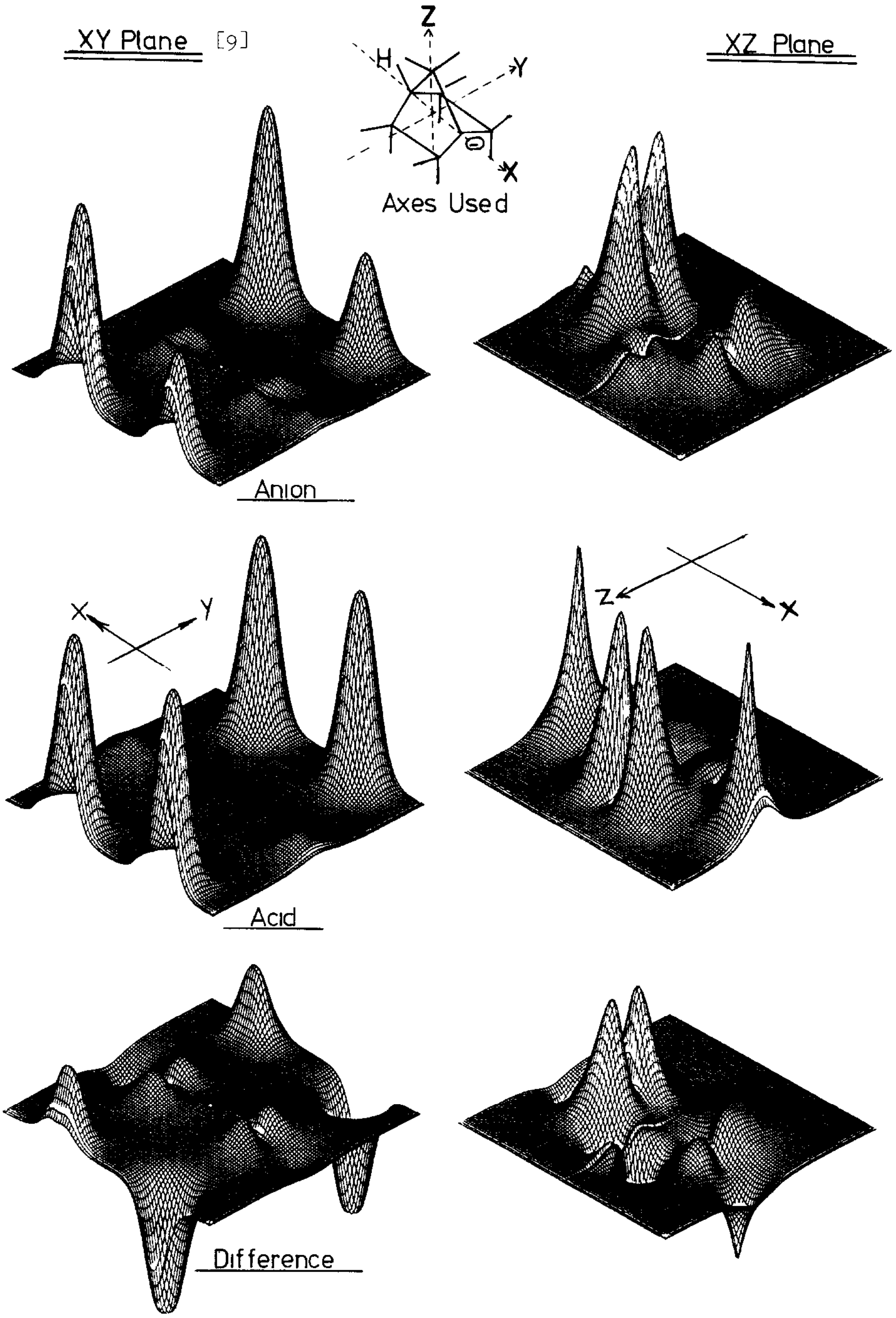
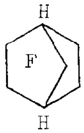
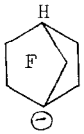
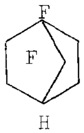
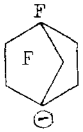


Figure 1. Electron densities in 1 and 1a [8]

TABLE 1

Calculated energies,* and energy differences

			
-329·1659	-328·3500	-356·1303	-355·3295
Differences ·8159		·8008	

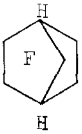
Difference between the two ionisation energies, Q = ·0151

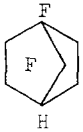
≐ 9Kcal

*Hartree unless otherwise stated.

TABLE 2

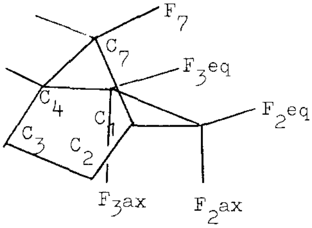
Calculated charges on various atoms in the molecules discussed





Position*	Acid	Anion	Differences	Differences	Acid	Anion
C_1	-·131	-·452	-·321	-·313	-·137	-·450
C_2	+·377	+·381	+·004	+·005	+·378	+·383
C_3		+·359	-·018	+·005	+·350	+·335
C_4		-·123	+·008	-·005	+·086	+·081
C_7	+·435	+·422	-·013	-·008	+·411	+·403
F_2eq	-·186	-·240	-·054	-·055	-·180	-·235
F_2ax	-·181	-·233	-·052	-·053	-·176	-·229
F_3eq		-·230	-·044	-·045	-·172	-·217
F_3ax		-·225	-·044	-·044	-·172	-·216
F_7	-·189	-·242	-·053	-·053	-·179	-·232
R	+·083	+·013	-·070	-·061	-·150	-·211
Acidic H	+·083				+·091	

*numbering as in



RESULTS

Calculations were performed for four molecular species 1, 1a, 2 and 2a. The energies calculated and the relevant differences are shown in Table 1. From these differences it may be estimated that 1 should have a pK_A 7 units higher than 2. Although this difference is apparently much too large, the difference between the protonation energies calculated (Q) is reasonable (experimental pK difference gives $\sim$ 7 Kcal, Q $\sim$ 9 Kcal) so that the calculated properties of the molecules may be assumed to be good approximations to nature.

The major point here is that the behaviour of 1 and 2 on deprotonation is very similar with regard to redistribution of charge. Table 2 displays the calculated charges on the atoms of the species studied, and it is easily seen from the 'differences' columns that the reorganisation of charge is very similar in both cases - at least at this rather crude level of analysis. In particular, only small amounts of charge are delocalised onto the 4H or 4F respectively (allbeit these both acquire more charge on ionisation than any other atom except C1).

The bulk of the redistributed charge, however, remains on C1 or is moved onto the fluorine atoms. This redistribution is illustrated for the highest occupied molecular orbitals in 1 and 1a in figure 1 . The results for 2 and 2a are similar. The three plots are, in descending order, for the anion (A) the acid (Ac) and the difference (A-Ac) between them. The geometry of the molecule is shown in the small inset, with axes marked also on the plots.

In summary, the acidity of these compounds is calculated to be mainly due to the powerful inductive effect of the fluorine atoms β to the anionic centre, but there is significant transfer of charge onto C4 and it's substituent. Surprisingly, the quantity of charge transfered, upon deprotonation, to (C4 + substituent) is insensitive to the nature of the substituent. This cast doubt upon the easy explanation of the role of the 4-substitutent in stabilising the anion, and suggests that destabilisation of the acid by an electronegative group at C4 is the more important factor in promulgating changes in acidity within this series of compounds.

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6 Quantum Chemistry Program Exchange, Chemistry Department, Room 204, Indiana University, Bloomington, IN 47401, U.S.A.

7 T. A. Hamor and M. J. Hamor, private communication. This work is in the press for J. Chem. Soc. Perkin Trans. II.

8 Following a referee's comment, it is pointed out that the HOMO's in 1 and 1a are of the same symmetries (in C_s).

9 The large peaks in the XY plane are due to electron density from the equatorial fluorines, not C_2, C_3, C_5, C_6.