An *Ab Initio* Study of Monofluorocyclohexadienyl Anions

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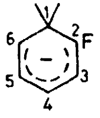
Ab initio calculations have been performed upon the title species, and the 4-31 G wavefunctions analysed by both the Mulliken and projection operator procedures. The results confirm the importance of the I_π repulsion effect on the proportion of isomers formed from a single substrate, but do not distinguish between this hypothesis and the alternative one, of a strongly activating effect of fluorine *meta* to the point of attack, as the dominant factor in determining relative rates of reaction of two different molecules.

WE have recently reported [1] our *ab initio* calculations on the cyclohexadienyl anion, whose central position in theories of nucleophilic aromatic substitution makes it an obvious first candidate for study amongst the anionic species derived from aromatic compounds. We now report our further investigations into the electronic structures and energies of the monofluorinated cyclohexadienyl anions. The importance of these lies in their use as models for the transition states which may arise in the nucleophilic displacement of fluorine from polyfluoroaromatic compounds. In addition to the *ortho*-, *meta*-, and *para*-isomers (I)—(III) we have made exploratory calculations for the *ipso*-form (IV) to study the effect of a fluorine α to the π system.



(I)

(II)

(III)

(IV)

METHODS

Calculations on the molecular species were performed using the POLYATOM [2] suite of programs, mounted on the CDC 7 600 computers of UMRCC; some of the atomic calculations were performed on the ICL 1906A machine at Birmingham, using the ATMOL [3] suite of programs.

Carbon and hydrogen atoms were fixed at the positions found for the cyclohexadienyl anion ($C_6H_7^-$), with C–F bond lengths being optimised at the 3G level (split 2,1 as before) before final calculations at the 4-31G level, using the basis sets of Pople *et al.*[4] Since the benefit of varying the scale factors appears to be small, standard scale factors were employed.

Population analyses were made using both Mulliken's method [5] and Roby's projection analysis procedure,[6,7] which is known to be much the more basis set independent.[1,6,8]

RESULTS AND DISCUSSION

The most immediate results are the energy quantities shown in Table 1. There are several points to note here. First, the highest filled state is very weakly bound, with that for the *para*-isomer (III) being actually slightly above the continuum level. This is probably due to the restricted basis used here, and in any case the main application of these calculations lies in solution reactions where solvation, gegenions, *etc.*, will render such states well bound.

Secondly, (I)—(III) all have the three topmost filled states with π symmetry; of the two deeper lying π-states, the deeper is in each case predominantly a fluorine *p*-orbital, interacting slightly with the π-orbital on the ring; the higher corresponds to the nodeless π-orbital in the cyclohexadienyl anion (*ca.* —0.377 Hartree), somewhat destabilised by an anti-bonding interaction with the fluorine *p*-orbital but stabilised by the nuclear charge of the fluorine. The descriptions of the remaining π states are more complex.

Of the σ states in (I)—(III), we draw attention to the lowest lying of all, which in each case corresponds to the fluorine 1*s* orbital, and to the states (ε_8 in each case) corresponding to the fluorine 2*s* orbital, since we shall refer to them in the discussion of the population analyses.

A third important feature is the calculated C–F bond lengths. Where the fluorine is bound to the π system [(I)—(III)], the calculated bond lengths are somewhat greater than usual, although not exceptionally so; in (IV), however, the bond length estimated (without optimisation of $\widehat{HCF}$) is 1.5 Å, which is extremely long for a C–F bond. There is no obvious reason why this should be so, but an unpublished fully optimised calculation, using an extended basis, on pyramidal CH_2F^- [9] indicates a similarly lengthened C–F bond. Internuclear repulsion may perhaps be a dominant factor here.

Fourthly, we comment upon the total energies of the species; as previously predicted,[10] the least stable of the three non-*ipso*-isomers is the *para*, followed by the *ortho*, with the *meta*-isomer the most stable. Of course, the least accurate calculation is that for the *ortho*-isomer, since we have not optimised the $\widehat{CCF}$ angle and this may well be important. Thus, the I_π repulsion explanation of isomer distribution in nucleophilic aromatic substitution is consistent with these calculations. However, the *ipso*-form is much more stable (by *ca.* 20 kcal mol^{-1}) than the other forms and we attribute this to the fluorine atom being able to exert to the full its beneficial σ inductive effect, without the countervailing disadvantage of the π repulsion effect. We speculate here that this strong effect may well go far towards explaining the preferential substitution of aromatic fluorine in situations where either fluorine or another halogen might be

TABLE 1

Energy quantities for the $C_6H_6F^-$ species calculated in this work

		ortho [b]		*meta* [b]		*para* [c]	*ipso* [d]
Total energy [a]		−329.562 42		−329.566 53		−329.555 26	−329.596 68
Nuclear repulsion energy		277.0597		276.6348		275.8256	274.7618
Kinetic energy		330.2208		330.1796		330.2144	330.0147
Virial ratio		−1.9980		−1.9981		−1.9980	−1.9987
Energy level		Energy		Energy		Energy	Energy
26	π	−0.001 58	π	−0.010 10	$4b_2$ (π)	+0.002 04	−0.039 19
25	π	−0.148 60	π	−0.149 28	$1a_2$ (π)	−0.156 24	−0.155 39
24	π	−0.250 90	π	−0.246 93	$3b_1$ (π)	−0.245 16	−0.266 94
23		−0.277 28		−0.273 77	$8b_2$	−0.262 54	−0.268 30
22		−0.307 44		−0.298 75	$13a_1$	−0.323 49	−0.299 28
21		−0.366 85		−0.365 24	$7b_2$	−0.365 01	−0.340 52
20		−0.377 64		−0.383 91	$2b_1$ (π)	−0.387 77	−0.360 28
19	π	−0.385 82	π	−0.389 55	$6b_2$	−0.388 96	−0.389 57
18		−0.405 54		−0.418 96	$12a_1$	−0.392 40	−0.404 93
17		−0.480 67		−0.460 53	$1b_1$ (π)	−0.472 66	−0.439 60
16	π	−0.488 19	π	−0.499 22	$5b_2$	−0.473 91	−0.444 35
15		−0.496 44		−0.506 23	$11a_1$	−0.491 38	−0.462 09
14		−0.516 98		−0.546 91	$10a_1$	−0.516 25	−0.518 20
13		−0.619 40		−0.624 21	$4b_2$	−0.625 19	−0.622 79
12		−0.647 50		−0.656 34	$9a_1$	−0.638 75	−0.637 63
11		−0.799 70		−0.800 94	$3b_2$	−0.807 31	−0.810 17
10		−0.818 66		−0.816 91	$8a_1$	−0.811 52	−0.810 96
9		−0.832 44		−0.933 61	$7a_1$	−0.933 27	−0.938 42
8		−1.415 52		−1.444 69	$6a_1$	−1.396 49	−1.314 65
7		−10.957 96		−10.961 46	$2b_2$	−10.983 06	−10.980 06
6		−10.978 58		−10.978 08	$5a_1$	−10.983 06	−10.990 17
5		−11.021 40		−10.983 37	$4a_1$	−11.013 39	−10.990 18
4		−11.021 99		−11.016 88	$3a_1$	−11.028 37	−11.033 61
3		−11.025 38		−11.029 23	$1b_2$	−11.028 44	−11.033 62
2		−11.065 14		−11.110 88	$2a_1$	−11.034 87	−11.091 06
1		−26.046 61		−26.075 20	$1a_1$	−26.032 40	−25.973 21

[a] Total energy for C_6H_5F in 4-31G basis is −329.0816, with C–F optimised to 1.365 Å; optimised C–F distances, *ortho* 1.35, *meta* 1.340, *para* 1.36, calculation for *ipso* 1.50 Å. [b] Energy levels not designated π are σ. [c] Energy level symmetries according to C_{2v}. [d] Reflection plane for *ipso* is not the same as for the others, and there are therefore *no* π orbitals here.

displaced.[11] We note here also that the geometry optimisation for the *ipso*-form is less complete than for the others, so that this energy difference is more likely to be an under- than an over-estimate.

TABLE 2

Mulliken population analyses for the heavy atoms in *o*, *m*, and *p*-fluorocyclohexadienyl anions

	Charge or bond order		
Atom or bond	*ortho*	*meta*	*para*
C(1)	−0.3255	−0.2943	−0.2964
C(2)	−0.2398 †	−0.3944	−0.3571
C(3)	−0.2027	0.4183 †	−0.1779
C(4)	−0.4172	−0.4418	−0.1498 †
C(5)	−0.1449	−0.1530	−0.1779
C(6)	−0.3779	−0.3516	−0.3571
F	−0.5156	−0.5029	−0.5301
C(1)–C(2)	0.6308	0.4951	0.6072
C(2)–C(3)	1.0874	1.0198	0.9550
C(3)–C(4)	0.6766	0.7305	0.7699
C(4)–C(5)	0.8801	0.6541	0.7699
C(5)–C(6)	1.0967	1.1126	0.9550
C(6)–C(1)	0.5620	0.6007	0.6072
C–F	0.2693	0.3898	0.3077

† Fluorine-bearing carbon.

We have carried out Mulliken population (Table 2) and Roby projection-operator based analyses (Table 3). For the present purposes we confine ourselves to discussion of the carbon skeleton and the fluorine atoms. We have not thought it proper to report on the analyses of the *ipso*-wavefunction, since the geometry is so poorly optimised.

In the Mulliken analysis, the most noteworthy features are the charges on the various atoms, and the C–F bond orders. The charges on carbon are of the order previously found for the unsubstituted anion, with the exception of the fluorine-bearing atom, where a positive charge is, not unexpectedly, found. Also, it is clear that

TABLE 3

Projection density population analysis for *o*-, *m*- and *p*- $C_6H_6F^-$ species

	ortho-F	*meta*-F	*para*-F
C(1)	9.0086	9.0079	9.0091
π only	1.7366	1.7299	1.7298
C(2)	8.3676 †	8.8649	8.8394
π only	1.5773	1.6113	1.5744
C(3)	8.7621	8.2983 †	8.7535
π only	1.4118	1.4185	1.3998
C(4)	8.9849	8.9908	8.5027 †
π only	1.7017	1.7148	1.7070
C(5)	8.7413	8.7384	8.7535
π only	1.3804	1.3779	1.3998
C(6)	8.8576	8.8377	8.8394
π only	1.5984	1.5703	1.5744
F	9.7998	9.7889	9.8020
π only	1.9845	1.9802	1.9910
C(1) + C(2)	1.5239	1.5485	1.5409
π only	0.0934	0.0910	0.0960
C(2) + C(3)	1.9699	1.9448	2.0040
π only	0.4410	0.4224	0.4470
C(3) + C(4)	1.8286	1.7978	1.8098
π only	0.2833	0.2849	0.2926
C(4) + C(5)	1.8468	1.8353	1.8098
π only	0.3107	0.2899	0.2926
C(5) + C(6)	1.9911	2.0090	2.0040
π only	0.8114	0.4619	0.4470
C(6) + C)1)	1.5434	1.5383	1.5409
π only	0.0933	0.0936	0.0960
C + F	1.0070	1.0425	0.9870
π only	0.0475	0.0662	0.0299

† Fluorine-bearing carbon atom.

a fluorine increases the negative charge on a β-carbon as compared to the value found in the absence of fluorine. The C–C bond orders are only slightly affected by the fluorine substitution, but the C–F bond, which is one of the strongest C–X bonds known,[12] has a very small bond order in all cases. The values of these indicate that the C(3)–F bond is the strongest, as expected, but that the C(2)–F bond is weaker than C(4)–F.

The Roby analysis, which is performed in terms of atomic orbitals,[7] not basis functions, is known to be much less basis-set dependent than the Mulliken procedure, and we have carried this through on (I)—(III) in the hope of getting a clearer idea of the relative effects of σ and π electronic factors. We note here that atomic populations can go up to 8 for a filled shell on an atom. Consequently, the atomic population is not to be viewed in the same light as is a Mulliken population; comparisons across the different species are, however, straightforward. Again, we discuss only the carbon framework and the fluorine atom.

We draw attention here firstly to the C–F bond populations, which now have a more reasonable magnitude in each case. Also, the order of these values (totals) is $m > o > p$, with most of this difference occurring in the π populations. Further, the total atomic population (η) on the fluorine is greatest in the *para-* and least in the *meta*-case, with the π contributions again being predominant. These values reflect the calculated bond lengths.

The populations on the fluorine-bearing carbon atoms show the strong bias in electron distribution towards C(2) and C(4) which was evident in the unsubstituted species, showing up as a greater population on C(4) [in (III)] than on C(2) [in (I)], with C(3) [in (II)] least populated.

That the total atomic charges shown in the Mulliken analyses are not unreasonable is shown by the relationship between the energies of the fluorine 1*s* (ε_1) and 2*s* (ε_8) eigenstates in (I)—(III) and the energies of the 1*s* and 2*s* states of isolated fluorine species (Table 4).

TABLE 4

Eigenvalues for fluorine species in 4-31G basis

	F^-		$F\cdot$	F^+
1*s*	−25.630 84		−26.300 26	−27.148 51
2*s*	−0.955 66		−1.463 03	−2.213 58
2*p*	−0.068 37	$2p^1$	−0.815 26	−1.384 82
		$2p^4$	−0.665 27	

Interpolation of the calculated eigenvalues of the orbitals ε_1 and ε_8 in (I)—(III) leads to the conclusion that charges of *ca.* −0.5 on fluorine are reasonable (ε_1, for example, comes about midway between the 1*s* energies of F· and F^-) with the fluorine atom in (II) bearing least charge, and that in (III) the most. [Interestingly, this comparison suggests that the fluorine in (IV) bears the greatest charge of all.]

The relevance of these calculations to nucleophilic aromatic substitution is that they permit an investigation of the effects of increasing fluorine substitution upon the ease of formation of Meisenheimer complexes and thus, by implication, of rates of nucleophilic substitution in different compounds. This is illustrated by the calculated values of the exotherm in the various reactions:

$$Ar + H^- \longrightarrow ArH^-$$

We have previously estimated this quantity for the reaction of benzene itself to be 6—12 kcal mol^{-1}, and, using the same value for the energy of H^- and a calculated energy for fluorobenzene (Table 1, footnote *a*), we have estimated this quantity for the isomers (I)—(IV) (Table 5).

TABLE 5

Exotherms for reaction $C_6H_5F + H^- \longrightarrow C_6H_6F^-$

Isomer formed	Calculated exotherm (kcal mol^{-1})
(I)	18
(II)	20
(III)	13
(IV)	40
Benzene + H^-	7

The most important point about these results is that they are all significantly more exothermic than the value estimated for the unsubstituted reaction, so that extra fluorines in a system are predicted to be activating towards nucleophilic aromatic substitution, in accord with experiment. Thus, it might be argued with Musgrave *et al.*[13] that in such reactions the beneficial effects of a fluorine atom on a π system outweigh the I_π disadvantage (that is, the repulsive effect between a fluorine lone pair and the ring π system) particularly in the case of fluorine in C(3). However, whilst this is probably true for fluorine in C(2) and C(3), the *general* argument is a difficult one, since (i) the results in Table 5 are differences of differences, and so doubly subject to error; (ii) the modelling assumption that Meisenheimer complexes are close to the transition state (Hammond principle) is only generally true, and will be less good for some substrates than for others; and (iii) the relevant energy must be dependent *both* upon the energy of the Meisenheimer complex *and* upon that of the ground state (a point made previously). This is important, because even amongst isomers, stabilities can differ significantly,[14] and, more generally, the assumption that ground-state effects will somehow cancel out (by being subsumed into the transition states?) cannot be true, except fortuitously.

This said, it is certainly true that our results can be interpreted as supporting a predominantly favourable influence of fluorine substituents *meta* to the point of attack, with *ortho*-fluorine being still beneficial and *para* being approximately neutral. However, it should equally be said that our results may be interpreted as supporting the alternative I_π theory. Here the I_π effect is regarded as predominant in determining isomer distributions, the main point of the argument being that a *para*-fluorine is destabilising and not neutral. Our calculated energies and the electron distributions clearly fall into line with this hypothesis. Until ground state (substrate) effects can be taken into account, a clear decision between these hypotheses is precluded.

Finally, two minor points may be made: first, the magnitudes of energy differences calculated here probably rule out any major influence on isomer distribution of the essentially second-order effects predictable by frontier orbital theory.[15] Secondly, it may be that our choice of H^- as nucleophile has unduly favoured the *ortho*-isomer (I), since this introduces the smallest possible internuclear repulsion at this position. The different values of the internuclear repulsion energies in Table 1 show that this effect might well be a large one. This would tend to equalise the effects of the *ortho*- and *para*-fluorines in the present case.

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