The Field-induced Resonance Effect

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Molecular orbital calculations at the *ab initio* 4-31G level have been used to investigate the magnitude of the experimentally proposed field-induced resonance effect. Calculations are reported of the increase in π-electron transfer induced by a dipole or pole between a substituent and a carbon–carbon double bond. This additional π-electron transfer is shown to be relatively small compared with the transfer found in the corresponding unperturbed substituted ethylene.

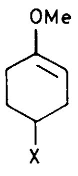
Some years ago, it was shown[1] that the i.r. intensity of the carbon–carbon stretching absorption in molecules (**1**) and (**2**) was enhanced when the substituent X had a significant field effect. This suggested an increase in π-electron interaction between the OMe and the double bond as represented, for example, by the resonance forms (**3**). The right-hand form in (**3**) was suggested to be stabilised, compared with the unsubstituted compound, by a dipole–charge interaction. A similar result was found for 3- and 4-substituted 1-chlorocyclohexenes. This was termed a field-induced resonance effect.

More recently,[2] similar effects have been demonstrated theoretically for conjugated unsaturated hydrocarbons such as butadiene and styrene, when polarised by dipoles and poles. Thus, the additional effect found in butadiene when polarised by HF can be represented by (**4**).

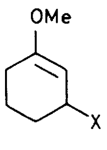
This differs from an earlier study[3] on analogous systems which suggested that the polarisation was of the π-system as a whole, rather than as represented by resonance canonical forms. Other results have subsequently been reported[4] to reflect such field-induced resonance effects. Nevertheless, carbon-13 results on the cyclohexenes did not confirm such an effect[5] and apparently such effects do not contribute significantly to overall electronic effects in disubstituted benzenes. Explanations of the carbon-13 and proton SCS observed in 4-substituted styrenes have[6] also included similar proposals.

We wished to look at the importance of field-induced resonance effects compared with the π-electron transfers found in the corresponding isolated molecules. In order to employ theoretical calculations at the split-valence basis, we used the relatively simple monosubstituted ethylenes as model compounds. We report an analysis of the polarisation of a series of monosubstituted ethylenes by a dipole (HF) and by a pole (NH_4^+).

All calculations were performed at the *ab initio* STO-3G or 4-31G level, using the Gaussian-80,[7] or Gaussian-82[8] programs and standard molecular geometries.[9] The π-electron populations were obtained from a Mulliken analysis.[10]



(**1**)



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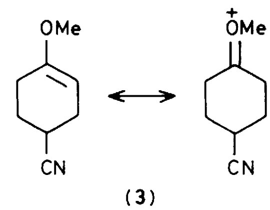

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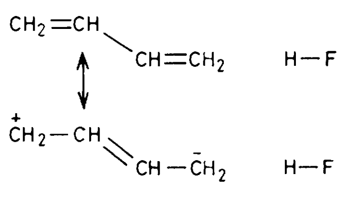

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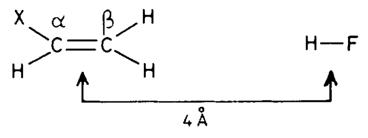
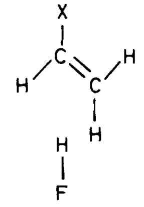
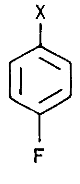


(**5**)



(**6**)



(**7**)

Results and Discussion

The results are given in Tables 1 and 2. The atomic electron populations are shown as differences from appropriate standards expressed in 10^{-3} electrons.

Table 1 shows the polarisation of the π-electron system of a variety of substituted ethylenes by HF. The geometry adoped in part A of Table 1 is as shown in (**5**). Table 1 also shows the π-electron populations for the corresponding isolated $XCH{=}CH_2$ molecules.[11] The figures given show the π-electron population at the β carbon atom ($\Delta q_{\Pi\beta}$) compared with ethylene (X = H) and the total π-electron transfer between the substituent X and the π-system of the vinyl group ($\Sigma\Delta q_{\Pi}$).

Similar results are shown in part B of Table 1 for polarisation with a geometry as in (**6**). For (**6**), the distance of the midpoint of the HF bond from the substituent X is taken to be equal to that in the corresponding *para*-fluorobenzene derivative (**7**).

The results for system (**5**) show that the additional π-charge transfer ($\Sigma\Delta q_{\pi}$) in the substituted ethylene caused by the HF is very small compared with the value in the isolated ethylene. The HF does induce some additional polarisation of the carbon–carbon double bond in ethylene itself ($q_{\pi\beta}$ = 1.014 electrons), but after allowance for this, little additional effect is seen in the substituted ethylenes over that in the isolated molecules.

The geometry used in part B of Table 1 corresponds to that in the corresponding *p*-fluorobenzene derivatives (**7**) and is close to that in the cyclohexenes (**1**). At this closer distance there is some

Table 1. Polarisation (4-31G) of the π-system of monosubstituted ethylenes (CH_2CHX) by HF (A, along CC axis, B in pseudo 4-fluoro-1-X-benzene geometry), Δq_π in 10^{-3} electrons, −ve indicates increase over 1.000 electrons for C_β or over 0.000 for Δq_π

	$\Delta q_{\pi\beta}{}^a$			$\Sigma\Delta q_\pi{}^a$		
A	Calc.[b]	Isol.[c]	Δ	Calc.	Isol.	Δ
NH_{2pl}	−188	−188	0	−116	−113	−3
OH[d]	−154	−154	0	−90	−89	−1
F	−56	−56	0	−62	−61	−1
Me	−45	−45	0	−9	−8	−1
H	0	0	0	0	0	0
CF_3	92	92	0	19	20	−1
CN	96	97	−1	31	33	−2
CHO[e]	64	66	−2	50	52	−2
NO_2	189	191	−2	72	75	−3
B	Calc.[f]		Δ	Calc.		Δ
NH_2	−190		−2	−119		−6
OH[d]	−158		−4	−94		−5
F	−55		1	−63		−2
Me	−43		2	−15		−7
H	0		0	0		0
CF_3	80		−12	12		−8
CN	93		−4	27		−6
CHO[e]	51		−15	46		−6
NO_2	171		−20	63		−9

[a] Carbon atom nearest to polarising group. [b] Corrected for values in ethylene, $q_{\pi\beta}$ = 1.014 electrons. [c] Isolated $CH_2{=}CHX$ in the reference. [d] OH bond *cis* to CC. [e] *s-trans*. [f] Corrected for values in ethylene, $q_{\pi\beta}$ = 1.012 electrons.

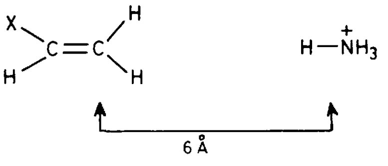
Table 2. Polarisation (4-31G) of the π-system of monosubstituted ethylenes (CH_2CHX) by $NH_4{}^+$ along CC axis. Δq_π in 10^{-3} electrons, −ve indicates increase over 1.000 electrons for C_β or over 0.000 electrons for $\Sigma\Delta q_\pi$

	$\Delta q_{\pi\beta}{}^a$			$\Sigma\Delta q_\pi{}^a$		
X	Calc.[b]	Isol.[c]		Calc.	Isol.[c]	
NH_{2pl}	−192	−188	−4	−124	−113	−9
OH[d]	−155	−154	−1	−95[a]	−89	−6
F	−56	−56	0	−65	−61	−4
Me	−45	−45	0	−14	−8	−6
H	0	0	0	0	0	0
CF_3	93	92	1	13	20	−7
CN	92	97	−5	25	33	−8
CHO[e]	59	66	−7	43	52	−9
NO_2	186	191	−5	65	75	−10

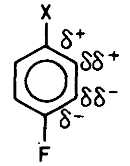
[a] Carbon atom nearest to polarising group. [b] Corrected for value in ethylene, $q_{\pi\beta}$ = 1.046 electrons. [c] Isolated $CH_2{=}CHX$ in the reference. [d] OH bond *cis* to CC. [e] *s-trans*.

small additional polarisation. The π-electron transfer to or from the substituent differs from that in the corresponding isolated ethylenes by 0.005—0.009 electrons in the expected direction, except in the fluoro derivative, where it is somewhat less. This later result is in accord with the lower polarisability of the fluorine atom substituent. For most substituents, however, the additional polarisation, the so-called field-induced resonance effect, is small compared with the normal resonance effect.

Table 2 shows results for the additional polarisation of the π-system of monosubstituted ethylenes caused by the $NH_4{}^+$ pole with a geometry as in (**8**). The results show an additional polarisation in the expected direction, but again the effect is relatively small for most substituents compared with the normal resonance interaction.



(**8**)



(**9**)

Overall then the results reported here support the concept of a field-induced resonance effect, but do indicate it to be relatively unimportant compared with normal resonance interactions. This is in accord with the rather small enhancements in i.r. intensity observed in molecules such as (**1**). It is important to note that the conclusion cannot be simply extended to substituted benzenes. Here, a substituent such as F can polarise the intervening π-system of the benzene ring, as indicated in (**9**), leading in turn to an additional induced π-electron transfer from X to the benzene π-system. Such a mechanism is not possible in the cyclohexenes (**1**) or the model systems listed here.

Acknowledgements

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