Tetrahedron. Vol. 31, pp. 3085 to 3088. Pergamon Press 1975. Printed in Great Britain

THE π-DONATING ABILITY OF HETEROATOMS IN α-SUBSTITUTED METHYL CATIONS

F. BERNARDI*
Laboratorio CNR dei Composti del Carbonio, Istituto di Chimica Organica, Universitá di Bologna, Viale Risorgimento, 4, Bologna, Italy

I. G. CSIZMADIA
Department of Chemistry, University of Toronto, Toronto, Canada

and

N. D. EPIOTIS*
Department of Chemistry, University of Washington, Seattle, Washington, U.S.A.

(*Received in UK* 23 *June* 1975; *Accepted for publication* 3 *July* 1975)

Abstract—An *ab initio* SCF geometry optimization on the simple cations $\overset{+}{C}H_2X$, with X = F, Cl, NH_2 and PH_2 has been performed at the split valence shell (4-31G) level. The computed optimum conformations correspond in each case to a structure in which all atoms lie in the same plane. Comparison of the computed charge distributions reveals that the third period heteroatom (Cl and P) is a better π electron donor than the corresponding second period analogue (F and N). This result parallels that obtained recently [*Can. J. Chem.* **53**, 1144 (1975)] for S and O in $\overset{+}{C}H_2OH$ and $\overset{+}{C}H_2SH$, but contradicts current notions based on assumed values of the C_π–X_π overlap integrals. It is shown here by explicit calculations of overlap integrals that these assumptions are not always correct. Furthermore, it is shown that arguments based only on overlap are necessarily incomplete since they neglect terms like the energy difference between the interacting orbitals which can play a dominant role. The relative importance of such terms is discussed for these species.

In the past three decades many basic, yet simple concepts regarding the structure and reactivity of organic molecules were developed on the basis of intuition rather than a quantitative theoretical approach. *Ab initio* computations,[1,2] which are now possible for molecules of chemical interest, coupled with PMO theory[3] as an interpretative tool, can be used to reexamine basic concepts which are currently highlighted in textbooks, monographs and the literature.

In this communication we shall examine the π-donating ability of heteroatoms in the simple systems $\overset{+}{C}H_2X$. Usually, it is assumed[4] that a second period heteroatom (e.g. F or OR) is a better π-electron donor than the corresponding third period heteroatom (e.g. Cl or SR), and because of this greater π-donating ability the second period heteroatom stabilizes the adjacent cationic center more than the corresponding third period analogue. However in a recent *ab initio* investigation[1] on $\overset{+}{C}H_2OH$ and $\overset{+}{C}H_2SH$ it was found that sulphur is a better π-electron donor than oxygen. In order to determine the π-donating ability of other pairs of heteroatoms, we have carried out *ab initio* computations on the $\overset{+}{C}H_2X$ cations with X = F, Cl, NH_2 and PH_2. In this paper we report theoretical results that contradict the current notion that a second period heteroatom is a better π-electron donor than the corresponding third period analogue.

Ab initio *results.* For comparative purposes the computations have been carried out with the same procedure used in the previous investigation[1] on $\overset{+}{C}H_2OH$ and $\overset{+}{C}H_2SH$. Therefore all computations here have been carried out with the Gaussian 70 series of programs,[5] using a split valence shell (4–3 1G) basis set.[6] For $\overset{+}{C}H_2F$[7], $\overset{+}{C}H_2Cl$ and $\overset{+}{C}H_2PH_2$ we have carried out an optimization with respect to all the geometrical parameters. For $\overset{+}{C}H_2NH_2$ only the C–N bond length has been optimized, while the remaining parameters have been kept fixed at the values obtained in the geometry optimization at a minimal basis set level.[8] The computed optimum conformation correspond for each system investigated to a structure in which all atoms lie in the same plane. The computed values of the various geometrical parameters are shown in Table 1.

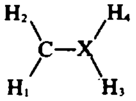
From inspection of these values the interesting point emerges that the C–X bond lengths do not vary significantly for heteroatoms of the same period, while the variation is significant in the corresponding CH_3X species (1·385, 1·427 and 1·474 Å for X = F, O and N respectively[9] and 1·784, 1·818 and 1·863 Å for X = Cl, S and P respectively[9] in CH_3X). Furthermore the C–X bond lengths of the $\overset{+}{C}H_2X$ systems are substantially shorter than those of the corresponding CH_3X systems, suggesting that in the cations the C–X bonds have significant double bond character. This is confirmed by the overlap population values for the various C–X bonds listed in Table 2.

A better understanding of the bonding properties of these cations can be obtained by a comparative analysis of the charge distribution. It has already been suggested[1] that an informative way to discuss the charge distribution in these species is to examine the charges of the two

Table 1. Geometrical parameters (bond lengths in Å and angles in degrees) computed at the 4-31G level for $\overset{+}{C}H_2X$ cations

Parameters[a] in $\overset{+}{C}H_2X$	X: NH_2	PH_2	OH[c]	SH[c]	F	Cl
r(C-X)	1·266	1·645	1·217	1·653	1·263	1·658
r(C-$H_{1,2}$)	1·103[b]	1·072	1·084	1·068	1·075	1·074
r(X-$H_{3,4}$)	1·038[b]	1·393	0·960	1·360	—	—
H_1CH_2	119·8[b]	117·7	122·1	117·3	126·1	120·7
CXH_3	121·85[b]	119·7	124·7	100·9	—	—

[a] The numbering scheme for the $H_2\overset{+}{C}$-X system is shown below



[b] Taken from Ref. 8

[c] Taken from Ref. 1

Table 2. Total, σ- and π-overlap populations of the carbon-heteroatom bonds in $\overset{+}{C}H_2$-X

Population	C-N	C-P	C-O	C-S	C-F	C-Cl
Total	0·3220	0·4468	0·2573	0·3002	0·2182	0·2600
σ	0·1271	0·2374	0·1067	0·1268	0·1207	0·1323
π	0·1949	0·2094	0·1506	0·1734	0·0974	0·1277

moieties CH_2^+ and X. These values are shown in Fig. 1.

Since the total charge of the CH_2^+ fragment prior to interaction is +1 and the total charge of the X fragment prior to interaction is 0, the total charges of the X moiety quoted in Fig. 1 represent also the amounts of electronic charge transferred to (or from) the CH_2^+ fragment as the result of the interaction with the various X fragments. It can be seen that the groups involving a third period heteroatom are all "good" electron donors, while among the groups containing a second period heteroatom only NH_2 shows a significant electron donating ability. In $\overset{+}{C}H_2OH$, in fact, the electron donation to CH_2^+ is negligible and in $\overset{+}{C}H_2F$ electron donation occurs in the opposite direction, i.e. from the already positive CH_2^+ moiety to the F atom.

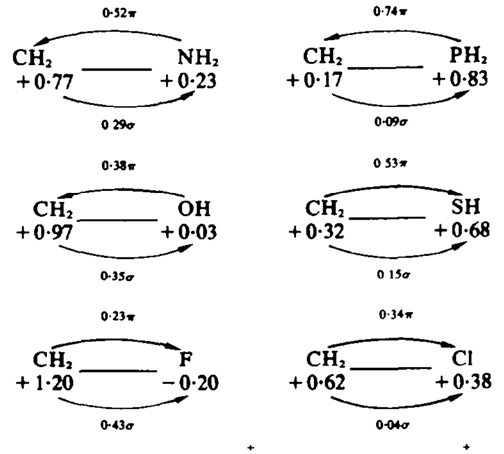


Fig. 1. Gross charges of the $\overset{+}{C}H_2$ and X moieties in $\overset{+}{C}H_2$-X, together with the σ and π electron transfers (values for $\overset{+}{C}H_2OH$ and $\overset{+}{C}H_2$-SH were taken from Ref. 1).

It is informative to investigate the details of such electron transfers. To this purpose we have also quoted in Fig. 1 the σ and π components of the total electron transfer between CH_2^+ and X. The values for the π-components have been computed from the gross orbital populations of the C_{2p_π} orbital. These values measure, in fact, the amount of electronic charge transferred from the X_{p_π} lone pair to the vacant C_{2p_π} orbital and therefore they are a measure of the π-donating ability of the various heteroatoms. The values for the σ-components are obtained as the difference between the values of the total and π electron populations. These σ populations represent the σ electron transfer to (or from) the $\overset{+}{C}H_2$ moiety.

The following interesting observations can now be made.

(i) With the X groups containing a third period heteroatom both the σ and π electron transfers occur in the same direction, i.e. from the heteroatom to the cationic center. The σ components of the electron transfer are in all the cases small and the electron transfer consists here almost entirely of π-electron donation from the heteroatoms. This π electron transfer is decreasing from P to Cl, i.e. it is in an inverse relationship with the change in electronegativity.

(ii) With the X groups containing a second period heteroatom there is always a π donation from the heteroatoms to the cationic center and the σ electron transfer is in the opposite direction. Going from N to F, as the electronegativity increases, the π-electron transfer decreases, while the σ term increases. However, with X = NH_2 and OH the π-component is the dominant term and the total electron transfer occurs from X to CH_2^+, while with X = F, the σ component becomes larger than the π-component and the total electron transfer occurs from CH_2^+ to F.

(iii) The computed π-donating abilities of the various heteroatoms toward an adjacent $\overset{+}{C}H_2$ center follow the sequence:

$$P > S \geqslant N > O > Cl > F.$$

Consequently, in contrast to current notions[4], a *third period heteroatom in such systems as* $\overset{+}{C}H_2$*-X is a better π-electron donor than the corresponding second row analogue.*

PMO analysis. Perturbation theory provides the framework for discussing orbital interactions. Here we shall try to provide a rationalization of the unexpected result stated above, namely that a third period heteroatom is a better π electron donor than the corresponding second row analogue and for this reason we shall focus our attention just on the interaction between the vacant $2p_\pi$ orbital (ϕ_B) of the CH_2^+ fragment and the p_π lone pair (ψ_A) of the adjacent heteroatom X.

Here ψ_A mixes with ϕ_B in a bonding combination and this amounts to an electron transfer, q, from ψ_A to ϕ_B approximated by the expression[10]

$$q = \frac{2H_{AB}^2}{\Delta E^2} = 2K^2\frac{S_{AB}^2}{\Delta E^2} \qquad (1)$$

where H_{AB} is the interaction matrix element between ψ_A and ϕ_B and ΔE is the energy separation between the vacant ϕ_B orbital and the ψ_A lone pair. In eqn (1) the usual approximation, $H_{AB} = K\ S_{AB}$, has been employed,† where K is a constant and S_{AB} is the overlap integral between ϕ_B and ψ_A. According to this simple equation, the electron transfer q increases either as the overlap between ϕ_B and ψ_A increases and or the .energy separation of the interacting levels decreases. We shall refer to the former as the overlap factor and to the latter as the energy factor.

In comparing a second period and a third period heteroatom, it will always be true that the energy factor favours greater electron transfer to the adjacent cationic center from the third period heteroatoms. This is necessarily so because the ionization potential of a lone pair of a second period heteroatom is always greater than that of a lone pair of a corresponding third period heteroatom. Typical first ionization potentials‡ and ΔE values are given in Table 3. The ΔE values have been computed from the values of the ionization potentials listed in the first column of Table 3 and from the orbital energy ϵ of the vacant $C_{p\pi}$ orbital of $\overset{+}{C}H_3$. This latter value ($\epsilon = -7{\cdot}66$ e.v.) has been obtained from an *ab initio* computation of CH_3^+ at the 4-3IG level with optimization of the C–H bond length.

Table 3. Typical first molecular ionization potentials (IP)[a] and related ΔE values[b]

Lone pair containing molecule	I.P. (eV)	ΔE (eV)
HF	15·77	8·11
HCl	12·80	5·14
H_2O	12·61	4·95
H_2S	10·48	2·82
H_3N	10·87	3·21
H_3P	10·10	2·44

[a] Taken from Ref. 12.

[b] $\Delta E = IP(X_{\text{lone pair}}) + \epsilon_{2p\pi}(\overset{+}{C}H_3)$.

Table 4. Two-center $C_{2p_\pi} - X_{p_\pi}$ overlap integrals (S_{AB}) computed at the optimum C–X bond length in $\overset{+}{C}H_2X$

	S_{AB}		
Bond	Set 1[a]	Set 2[b]	Set 3[c]
C–N	0·2596	0·2596	0·2454
C–P	0·2442	0·2434	0·2355
C–O	0·2169	0·2169	0·2031
C–S	0·2120	0·2106	0·2017
C–F	0·1680	0·1680	0·1571
C–Cl	0·1802	0·1786	0·1703

[a] Minimal SCF atomic orbitals.

[b] Single STO with exponential parameters from Clementi and Raimondi.

[c] Single STO with exponential parameters from Slater rules.

The overlap integral S_{AB} can be computed for the *al initio* optimized geometry of $\overset{+}{C}H_2$-X. Typical results are given in Table 4. We report here three sets of two-center overlap integrals computed using three different types of atomic orbitals: (i) SCF atomic orbitals from a minimal basis set of Slater type functions (STO), with the exponential parameters optimized by Clementi and Raimondi;[12] (ii) single Slater atomic orbitals (STO) with the exponential parameters optimized again by Clementi and Raimondi[13] and (iii) single Slater atomic orbitals, with the exponential parameters given by the Slater's rule. In all cases, the overlap factor favours Cl over F, it does not distinguish between S and O, and it favours N over P.

The combination of the energy and overlap factors indicate unequivocally that the π-electron transfer to the carbocationic center $\overset{+}{C}H_2$ will be larger for Cl than for F, and for SH than for OH and these predictions are in agreement with the *ab initio* results reported in Fig. 1. In the case of NH_2 and PH_2 the two factors act in opposite directions, since the energy factor favours P, but the overlap factor favours N. Since our *ab initio* results (see Fig. 1) show that the π electron transfer is greater for P than it is for N, we must conclude that in the PMO terminology the energy factor in this case is dominant over the overlap factor.

The same line of reasoning can be used also for discussing the π stabilization of the cationic center due to the conjugative interaction with the adjacent heteroatom. For nondegenerate orbitals, the π stabilization energy (SE) resulting from such an interaction is given by the expression

$$SE = 2\frac{H_{AB}^2}{\Delta E} = 2K^2\frac{S_{AB}^2}{\Delta E} \qquad (2)$$

where the various symbols have been defined in connection with eqn (1). Again the combination of the energy and overlap factors indicate unequivocally that Cl and SH will stabilize the carbocationic center more than F and OH, respectively and these predictions are in good accord with the experimental results of Taft *et al.*[13] Again, from such a qualitative approach, a clear prediction cannot be made for the case of $X = NH_2$ and PH_2, since the two factors act in opposite directions. This approach could be used again for rationalizing the experimental result, but unfortunately only the stabilization energy of $\overset{+}{C}H_2$-NH_2 is available.[13]

CONCLUSIONS

To summarize, the current notion that a second period heteroatom is a better π-electron donor than the third period analogue and that F and OR are correspondingly better π stabilizing groups than Cl and SR with respect to an adjacent carbocationic center are in contradiction with theoretical results. This current notion is based on the assumption that the two center π-overlap integrals $C_{2p_\pi} - X_{p_\pi}$ are larger when X is a second period heteroatom. As we have already seen this assumption is not supported by the explicit calculations of the overlap integrals for F and Cl, and 0 and S.

In addition, arguments based only on overlap are necessarily incomplete since they neglect the ΔE term in the denominator of eqns (1) and (2). In fact ΔE the difference between the energy of a filled orbital and the energy of an empty orbital, is important in all processes where charge transfer is taking place. We have, in fact,

---

†Other approximations of the matrix element are also possible.

‡The values of all molecules except HF were determined by a photoionization method, while the value for HF was determined by a retarding potential method:[11]

shown that it is the energy factor which dictates the trend of the π-donating ability for N and P, while the overlap factor acts in the opposite direction.

In view of the results presented here it becomes very interesting to reexamine those cases where a superiority of F over Cl or of OR over SR as conjugative stabilizers on an adjacent cationic center was postulated in order to account for the experimental observations. For example chloromethyl ethyl ether hydrolizes in aqueous dioxane about 1600 times faster than chloromethyl sulphide.[14] The reaction was assumed in both cases to proceed *via* a carbonium ion intermediate by a unimolecular mechanism and the effect of substituents on the rates was accounted for on the basis of the assumption that RO- stabilizes an adjacent carbocationic center more than RS- through a greater conjugative effect. In view of the present results, it is clear that, much remains to be done before a satisfactory understanding of the mechanism of such reactions is achieved.

Acknowledgements—One of us (F.B.) acknowledges useful discussions with Professors A. Mangini and G. Modena on this subject. The authors would like to thank Dr. M. Guerra for the computation of the overlap integrals listed in Table 4.

REFERENCES

[1] F. Bernardi, I. G. Csizmadia, H. B. Schlegel and S. Wolfe, *Can. J. Chem.* 53, 1144 (1975).

[2] For comprehensive theoretical studies of carbocations, the reader should consult: L. Radom, J. A. Pople, V. Buss and P. von R. Schleyer, *J. Am. Chem. Soc.* 94, 5935 (1972); and other papers in this series.

[3] The fundamentals of perturbation theory may be found in any quantum mechanic text. Applications to quantum chemistry are particularly well represented in E. Heilbronner and H. Bock, *Das Huckel MO Modell und Seine Anwendung*, Verlag Chemie, Weinheim, Bergst (1968); R. Hoffmann, *Accounts Chem. Res.* 4, 1 (1971).

[4] C. C. Price and S. Oae, *Sulphur Bonding*. Ronald Press, New York (1962).

[5] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton and J. A. Pople, *Quantum Chemistry Program Exchange*. Indiana University, Bloomington, Ind.

[6] R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.* 54, 724 (1971).

[7] The optimized geometry at a minimal basis level has already been published, see Ref. 8.

[8] W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle and J. A. Pople, *Progr. Phys. Org. Chem.* 11, 175 (1974).

[9] All the data, except r(C–P), have been taken from H. J. Bowen *et al. Compilers, Tables of interatomic distances and configuration in molecules and ions*. Special Publication No. 11. The Chemical Society, London, 1958. For r(C–P), see T. Kojima, E. L. Breig and C. C. Lin, *J. Chem. Phys.* 35, 2139 (1961).

[10] N. D. Epiotis, *J. Am. Chem. Soc.* 95, 3088 (1973).

[11] "*Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions*". National Bureau of Standards, NBS 26 (1969).

[12] E. Clementi and D. L. Raimondi, *J. Chem. Phys.* 39, 2686 (1963).

[13] R. W. Taft, R. H. Martin and F. W. Lampe, *J. Am. Chem. Soc.* 87, 2490 (1965). The stabilization energies quoted here refer to total stabilization energies.

[14] H. Bohme, H. Fischer and R. Frank, *Liebigs Ann.* 54, 563 (1949).