JOURNAL
OF
THE CHEMICAL SOCIETY

PERKIN TRANSACTIONS II
Physical Organic Chemistry

# An INDO Molecular Orbital Study of [1,3] π Interactions in 2-Substituted Allyl Cations

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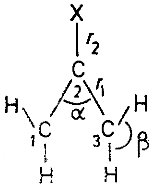
The INDO molecular orbital technique, including a partial geometry search, has been applied to three 2-substituted allyl cations and the parent allyl cation. It is deduced that electron-releasing substituents favour π bonding between the terminal carbons. The 2-oxidoallyl species is found to represent an extreme example of this effect, the [1,3] π interaction being so pronounced that 2-oxidoallyl appears to be best described as a monohomocyclopropenone.

MUCH experimental[1] and theoretical[2] work has been devoted to determining the importance of the [1,3] π interaction in allyl cations, although only alkyl substituents appear to have been considered to date. After some initial disagreement, quantum mechanical calculations and experimental measurements, notably $^{13}C$ n.m.r. chemical shifts, now seem to suggest that in these cases the [1,3] interaction is not significant. The single exception to be discovered is Katz's cyclobutenyl cation[1a] in which geometric constraints do appear to cause a marked increase in [1,3] π bonding.



(I)

a ; $X = O^-$
b ; $X = OH$
c ; $X = H$
d ; $X = NO_2$

Since π interaction between the termini of an allyl cation would be expected to cause a decrease in electron density on the central carbon,† it might be predicted that an electron-releasing substituent attached to this carbon would favour [1,3] bonding. Accordingly the allyl cations (Ia—d) were investigated using the INDO[3] molecular orbital technique. A partial geometry search was carried out in each case, the energy being minimized with respect to bond lengths $r_1$ and $r_2$ and angles α and β. Trial calculations showed that $r_1$ and $r_2$ were essentially independent within 0·1 Å of their equilibrium values; they were not, therefore, treated iteratively. The angles α and β were strongly interdependent, however, and hence were optimized simultaneously by taking sections through the α *vs.* β *vs.* energy surface and interpolating. The method is exemplified by the results for 2-oxidoallyl (Ia) depicted in Figure 1. The solid line in graph A connects the minima of the other curves; its turning

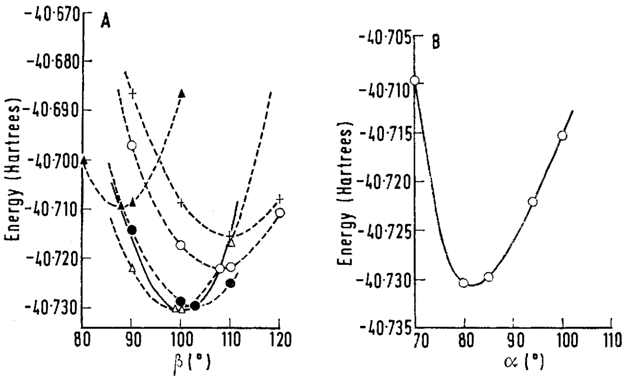


FIGURE 1 A. Graphs of β against energy for various values of α: +, α = 100°; ○, α = 94°; ●, α = 85°; △, α = 80°; ▲, α = 70°. B. Graph of α against energy at optimum β

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† This is because the system is tending towards a limit of the cyclopropenyl cation in which each carbon bears 1/3 of the positive charge.

[1] (*a*) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, 1964, **86**, 1600; (*b*) G. A. Olah and M. B. Comisarow, *ibid.*, p. 5682; (*c*) R. H. Griffin and J. G. Jewett, *ibid.*, 1970, **92**, 1104; (*d*) G. A. Olah, P. R. Clifford, Y. Halpern, and R. G. Johanson, *ibid.*, 1971, **93**, 4219.

[2] M. Simonetta and E. Heilbronner, *Theor. Chim. Acta*, 1964, **2**, 228; D. T. Clark and D. R. Armstrong, *ibid.*, 1969, **13**, 365.

[3] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

point represents the optimum value of β and the corresponding best energy. The optimum value of α is the minimum of curve B.

It should be noted that, in order to reduce the number of degrees of freedom in the geometry search, the terminal hydrogens were restricted to symmetric positioning about the C–C bonds; although a lower energy might well be found for an asymmetric arrangement, this was not considered to be of primary interest to the present work. The interdependence of angles α and β can probably be attributed to H–H repulsion at small values of α.[4d]

The equilibrium geometries calculated in this manner are listed in Table 1. A constant value of 1·08 Å was assumed for the terminal C–H bond distances. Already it will be seen that the steadily decreasing value of the C–C–C internal angle (α) with greater electron availability at C(2) is suggestive of increasing [1,3] bonding. But more direct evidence is available. The extent of [1,3] π interaction can be calculated directly from the product of the overlap integral between the $p\pi$ orbitals on the terminal carbons and the corresponding density matrix element[3] [equation (1) where $S_{ij}$ is the overlap

TABLE 1

Equilibrium geometries

| | (Ia) | (Ib) | (Ic) | (Id) |
|---|---|---|---|---|
| $r_1$(Å) | 1·395 | 1·372 | 1·365 | 1·372 |
| $r_2$(Å) | 1·300 | 1·352 | 1·08 | 1·446 |
| α(°) | 81·5 | 104·7 | 110·9 | 112·3 |
| β(°) | 100·1 | 111·6 | 111·9 | 112·8 |

$$D_{ij}(\pi) = S_{ij}(p\pi) \, . \, P_{ij}(p\pi) \qquad (1)$$

integral between $p\pi$ orbitals on atoms $i$ and $j$ and $P_{ij}$ is the density matrix element]. $D_{ij}$ Is then proportional to the electronic population of the π bond between atoms $i$ and $j$. The values of $D_{13}$ listed in Table 2 can be seen in perspective when compared with the value of $D_{12} = 0{\cdot}1831$ for the parent allyl cation (Ic).

It is perhaps worth noting that the two components of the [1,3] π interaction can be given some physical significance; since the overlap integral $S_{ij}(p\pi)$ is a function of the distance between the atoms $i$ and $j$ it can be regarded as the *geometric* component whereas $P_{ij}(p\pi)$ is a measure of the population of the orbitals under consideration and is thus the *electronic* component. One can now distinguish between the situation in the cyclobutenyl cation[1a] and that in the series of allyl cations considered here. In the former case an external 'mechanical' constraint, the methylene group of the four-membered ring, forces C(1) and C(3) together, thereby increasing $S_{13}(p\pi)$ and hence $D_{13}(\pi)$. In the allyl cations (Ia—d) there is no such constraint but it is found that, nevertheless, the optimum distance between the terminal carbons decreases as the 2-substituent becomes more electron releasing. This change of geometry can be rationalized in terms of increasing favourability of the [1,3] π interaction. The same rationale can explain the observation that the electron population $P_{13}(p\pi)$ increases along the series (Id) ⟶ (Ia). The quantity $D_{13}$ represents the combination of these two effects.

TABLE 2

π Charge distribution and values of $D_{13}$ for allyl cations (Ia—d)

| | (Ia) | (Ib) | (Ic) | (Id) |
|---|---|---|---|---|
| $\zeta_1$(e) | +0·251 | +0·049 | −0·011 | −0·049 |
| $\zeta_2$(e) | +0·174 | +0·429 | +0·506 | +0·526 |
| $D_{13}$ | 0·0859 | 0·0324 | 0·0243 | 0·0218 |

It is also interesting to note that the π charge on the central carbon atom ($\zeta_1$) becomes more positive as the substituent becomes more electron releasing whereas the π charge on the terminal carbons ($\zeta_2$) becomes less positive. This is consistent with the π molecular orbitals of the allyl cation tending towards those of the cyclopropenyl cation as the [1,3] π bond becomes stronger.

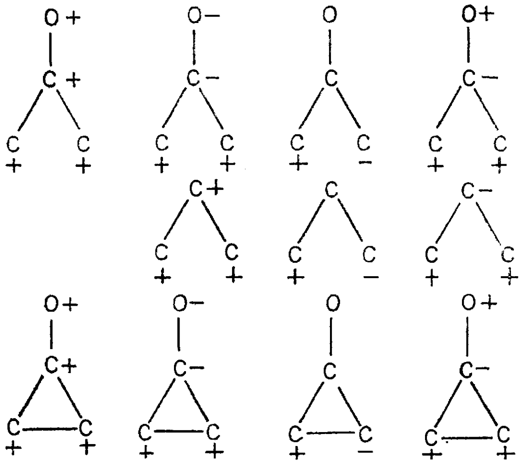

FIGURE 2 Phases of the π MOs of 2-oxidoallyl, allyl, and cyclopropenone

Perhaps the most noteworthy results are those for 2-oxidoallyl (Ia) which can be seen as an extreme example of the general principle developed here. The 2-oxidoallyl species has been the subject of much interest recently[4,5] particularly with respect to its possible formation by the ring opening of cyclopropanone. The present calculations suggest that the substantial electron donation by O⁻ leads to such a marked [1,3] π interaction that the species is best considered to be a monohomocyclopropenone.[6] Strong support for this description comes from inspection of the π molecular orbitals of 2-oxidoallyl in the geometry described here. It is found that $\pi_2$ (the highest occupied π molecular orbital)

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[4] (*a*) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1954, 1201; (*b*) R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 1475; (*c*) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, 1970, **92**, 3854; (*d*) J. F. Olsen, S. Kang, and L. Burnelle, *J. Mol. Structure*, 1971, **9**, 305; (*e*) A. Liberles, A. Greenberg, and A. Lesk, *J. Amer. Chem. Soc.*, 1972, **94**, 8685.

[5] R. C. Cookson and M. J. Nye, *J. Chem. Soc.*, 1965, 2009; K. Schaffner, *Adv. Photochem.*, 1966, **4**, 81; P. J. Kropp, *Organic Photochem.*, 1967, **1**, 1; N. J. Turro, *Accounts Chem. Res.*, 1969, **2**, 25; H. E. Zimmerman, *Angew. Chem. Internat. Edn.*, 1969, **8**, 1.

[6] For the concept of homoaromaticity see S. Winstein, *Chem. Soc. Spec. Publ.*, 1967, **21**, 5; *Quart. Rev.*, 1969, **23**, 141.

no longer has the same relative phases as the corresponding MO of the parent allyl cation (Ic) but that all the $\pi$ MOs of 2-oxidoallyl are analogous to those of cyclopropenone. Increasing the value of the angle $\alpha$ causes reversion to the parent allyl type molecular orbitals.

TABLE 3

LCAO Coefficients for the $\pi$ MOs of 2-oxidoallyl

| | $C_1$ | $C_2$ | $C_3$ | O |
|---|---|---|---|---|
| $\pi_1$ | 0·4651 | 0·6392 | 0·4651 | 0·3985 |
| $\pi_2$ | 0·3981 | −0·0656 | 0·3981 | −0·8239 |
| $\pi_3$ | 0·7071 | 0·0 | −0·7071 | 0·0 |
| $\pi_4$ | 0·3539 | −0·7662 | 0·3539 | 0·4030 |

In addition the $\pi$ charges in 2-oxidoallyl are found to be intermediate between those calculated for 2-oxidoallyl with a larger C–C–C internal angle and those of cyclopropenone.

The energy calculated for singlet 2-oxidoallyl in the geometry reported here is 193 kJ mol$^{-1}$ lower than that from the INDO results recently reported [4e] for the species, although it is doubtless still too high with respect to the energy calculated for cyclopropanone.

Although more rigorous calculations (particularly including configuration interaction) might predict different equilibrium geometries for the allyl cations considered here, it seems justifiable to conclude that the calculated increase in [1,3] $\pi$ bonding with greater electron availability at the central carbon is qualitatively correct.

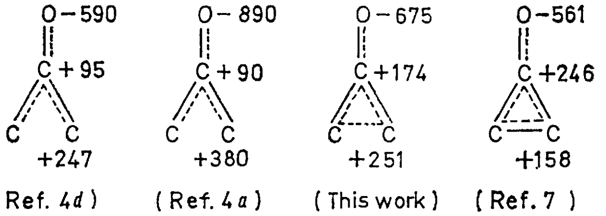

FIGURE 3 Comparison of charges in 2-oxidoallyl from present calculations with those from past work and those of cyclopropenone. Units are $10^{-3}$e

I thank Dr. H. M. R. Hoffmann for helpful discussions and the S.R.C. for financial support.

[3/1337 *Received, 25th June,* 1973]

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[7] D. J. Bertelli and T. G. Andrews, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 5280.