Ab initio Molecular Orbital Calculations on Allylic Anion–Olefin Interactions

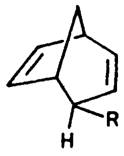
By **John M. Brown,*** The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY
Robert J. Elliott and **W. Graham Richards,** Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

Interaction of an allylic anion with an olefin has been studied by *ab initio* STO 3G (Gaussian 76) calculations. Approach of the two entities leads to an increase in the total energy of the system, but in all the configurations examined the HOMO energy decreases down to a separation of 2.4 Å. The calculations are used as a model to evaluate the extent of homoaromatic stabilisation in the bicyclo[3.2.1]octa-3,6-dien-2-yl anion (2). It was found that the bicyclic anion has a HOMO energy lower than that of an isolated allyl anion. Sphere-charge calculations suggest that negative charge is delocalised on to the ethylenic fragment of anion (2). These calculations provide support for the original postulate of long-range delocalisation in anion (2), and refute the recent claims by Grutzner and Jorgensen, and by Mayr, Schleyer, and their co-workers, that stabilisation of homoaromatic anions is due to an inductive effect.

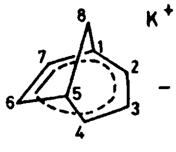
SOME years ago it was demonstrated that bicyclo[3.2.1]octa-2,6-diene (1a) exchanged hydrogen for deuterium at the allylic position 1×10^4—3×10^4 times faster in basic dimethyl sulphoxide than did model compounds.[1] It was then suggested that charge delocalisation to the remote double bond giving (2) was responsible for the disparity. The interpretation was apparently reinforced by the ^{1}H n.m.r. spectrum of the anion derived by reduction of *exo*-4-methoxybicyclo[3.2.1]octa-2,6-diene (1b) which showed that 6- and 7-H were shielded by over 2 p.p.m. relative to the parent hydrocarbon.[1] Related effects were found for anion (3) and here additional stabilisation over its mono-olefinic analogue (4) was observed.[2]

At the time of publication these results were readily interpreted as homoaromatic stabilisation,[3] then adequately supported by simple and extended Hückel one-electron calculations. Recent work has made the conclusion less clear-cut, however. The diphenyl carbanion (5) shows appreciable shielding of 6- and 7-H in its ^{1}H n.m.r. spectrum but very little stabilisation adjudged by the similarity of deprotonation rate of its 4*H*-conjugate acid and model compounds.[4] Tetracyclo-[3.3.1.1^{3,9}.0^{2,4}]dec-6-ene (6) does not show an enhanced rate of deprotonation at the 8-position in basic media,[5] suggesting that its anion is not stabilised by the remote cyclopropane. Carbanion (7) cannot be formed even under forcing conditions, and MINDO/3 calculations suggest that it is pyramidal with little or no conjugative stabilisation.[6] Cyclohexadienyl anion, in principle the simplest homoaromatic anion, has in *ab initio* calculations at the STO-3G level a near planar energy minimum,[7] the other minimum on the potential-energy surface corresponding to the isomeric bicyclohexadienyl anion (8) with a bridging cyclopropyl bond length of 1.608 Å. The latter is 142 kJ mol^{-1} above the ground state.

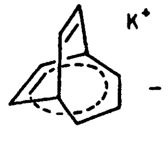
Neither experimental nor theoretical tests support the existence of homoaromaticity in neutral molecules. It is generally the case that through-bond interactions complement through-space interactions, this being supported by photoelectron spectroscopy and by *ab initio* calculations.[8] In the series of trienes with poten-



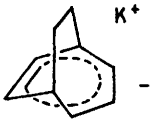
(1a) R = H
(1b) R = OCH$_3$



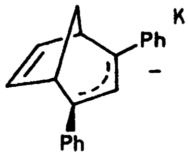
(2)



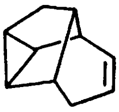
(3)



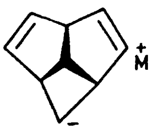
(4)



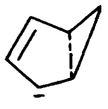
(5)



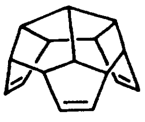
(6)



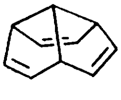
(7)



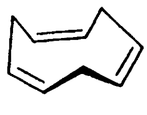
(8)



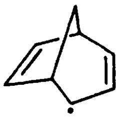
(9)



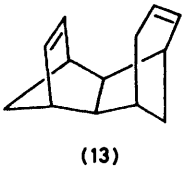
(10)



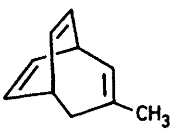
(11)



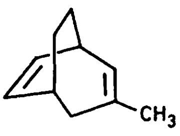
(12)



(13)



(14)



(15)

tial homoaromatic character represented by hexaquinacene (9) triquinacene (10), and cyclonona-1,4,7-triene (11),[9] structural distortions minimise overlap of π-bonds, so that repulsion between filled orbitals overrides any contribution from delocalisation. Even the radical (12) is not homoconjugated since the proportion of spin-density transferred to C-6 and -7 is very small and the e.s.r. hyperfine coupling constants are consistent with a classical allyl radical structure.[10]

These results suggest that the initial claims of long-range delocalisation in (2) and (3) merit re-examination. Two recent papers [11,12] are concerned with calculations on these anions using semi-empirical procedures (MNDO [11] or MINDO/3 [12]) to determine the ground-state geometry and then computing orbital energies by *ab initio* methods at the STO-3G level. The conclusions are very similar. Mayr, Schleyer, and their co-workers state that the 'bicyclo[3.2.1]octa-3,6-dien-2-yl anion is clearly not a bishomoaromatic system' and 'comparisons of C-2–C-7 overlap populations in different ions do not indicate any special stabilising interaction.' Gutzner and Jorgensen suggest that 'homoaromaticity is insignificant for hydrocarbon anions.' Both groups of workers consider that the increased stabilisation of (2) and (3) relative to anions lacking the double bonds is a consequence of induction despite the fact that these calculations only predict half the observed stabilisation; 13.8 [17.5] [12] *versus* 28.8 kJ mol^{-1} for (2) and 24.2 *versus* 42 kJ mol^{-1} for (3). They concur in suggesting that little mixing of the allyl HOMO and olefinic LUMO occurs.

The work as described raises a number of questions, since the origin of experimentally observed stabilisation in (2) and (3) is not clarified. Semi-empirical methods, which failed to detect any stabilisation in (2) or (3), were used to establish the ground-state anion geometry. Since homoaromatic interactions are very sensitive to structure and may require considerable distortion of the molecular framework,[13] this implies that the *ab initio* calculations may have been performed on inappropriate geometries. The claim of stabilising inductive effect is puzzling. The component of inductive stabilisation is in fact likely to be rather small. Values of σ_I between 0.05 and 0.09 for a vinyl group are quoted.[14] Since (1a) is deprotonated 10^4 times faster than cyclohexene, this indicates a reaction constant ρ_I of between 45 and 80 for the effect of β-substituents on allyl anion formation which seems at variance with commonsense. Furthermore, deprotonation of (13) is only weakly facilitated by the remote double bond.[15] If an inductive effect were operative the anion should be strongly stabilised since the latter would not be strongly dependent on olefin geometry. Hydrocarbons (14) and (15) undergo selective hydrogen isotope exchange at C-4 in basic media.[16] The isomeric allylic anions formed by deprotonation of the methyl group might predominate if only inductive effects were important, as they possess less destabilising alkyl substituents. Because of these doubts and qualifications we have carried out further calculations as described.

RESULTS AND DISCUSSION

Calculations have been carried out using *ab initio* STO 3G methods (Gaussian/76) [17] on the perturbation of allyl anion by ethylene as a function of their separation and relative orientation. Decreasing the distance between the two species causes considerable changes in overall energy and also strongly affects the allyl HOMO and olefin LUMO levels as shown in Figure 1. In each case the HOMO becomes more stabilised whilst the LUMO increases in energy. The total energy of the molecular system starts to rise sharply below *ca.* 2.8 Å, since below that distance closed-shell repulsions become critical and effectively over-ride favourable orbital interactions. It is a general artefact of minimal basis set *ab initio* calculations on carbanions that the HOMO energy is positive. Whilst this is clearly incorrect, the information on *relative* orbital energies, and the effects of interaction, should be tenable.

Consider first the coplanar approach A leading to π-interaction.* The HOMO energy decreases gradually with distance down to 2.8 Å and more sharply at closer approaches, this being accompanied by a substantial increase in LUMO energy. When the fragments approach at an angle of 60°, as in B, there is little interaction above 2.8 Å separation but below that distance HOMO stabilisation is apparent. At 2.4 Å [a rather similar geometry and energy to (2) with no skeletal distortion] there is less stabilisation than for π-interaction, but the HOMO decreases in energy rapidly as the internuclear distance decreases. The LUMO destabilisation is similar to that observed in A. For σ-approach C, there is a more dramatic change with decreasing internuclear separation, associated with a rather sharp minimum in HOMO energy at 2.4 Å. Destabilisation of the LUMO is here more pronounced at short internuclear distances.

These calculations indicate the sensitivity of allylic anion–olefin interactions to molecular geometry. This requires that computations must be carried out for a range of internal distances and bond angles before any conclusions about the existence or non-existence of homoaromatic stabilisation in a particular anion may be made. It is clear that the HOMO and LUMO are strongly affected and it cannot be said that, 'interaction between empty and occupied orbitals is insignificant' or that the 'increase in energy of the HOMOs as the anions become more saturated results from mixing between the allylic HOMO and σ-bond orbitals of the bridges' [for (2), (3) and analogues].

Neither Mayr and Schleyer nor Grutzner and Jorgensen presented orbital energies for (2) and further calculations have been carried out to define these at their equilibrium geometry. Results are shown in Figure 2 by comparison with an isolated allylic anion and olefin. The low energy of the HOMO and high energy of the LUMO in

---

* The calculations suggest a strongly destabilising H–H interaction between the fragments, responsible for the steep rise in energy as the distance between the fragments diminishes.

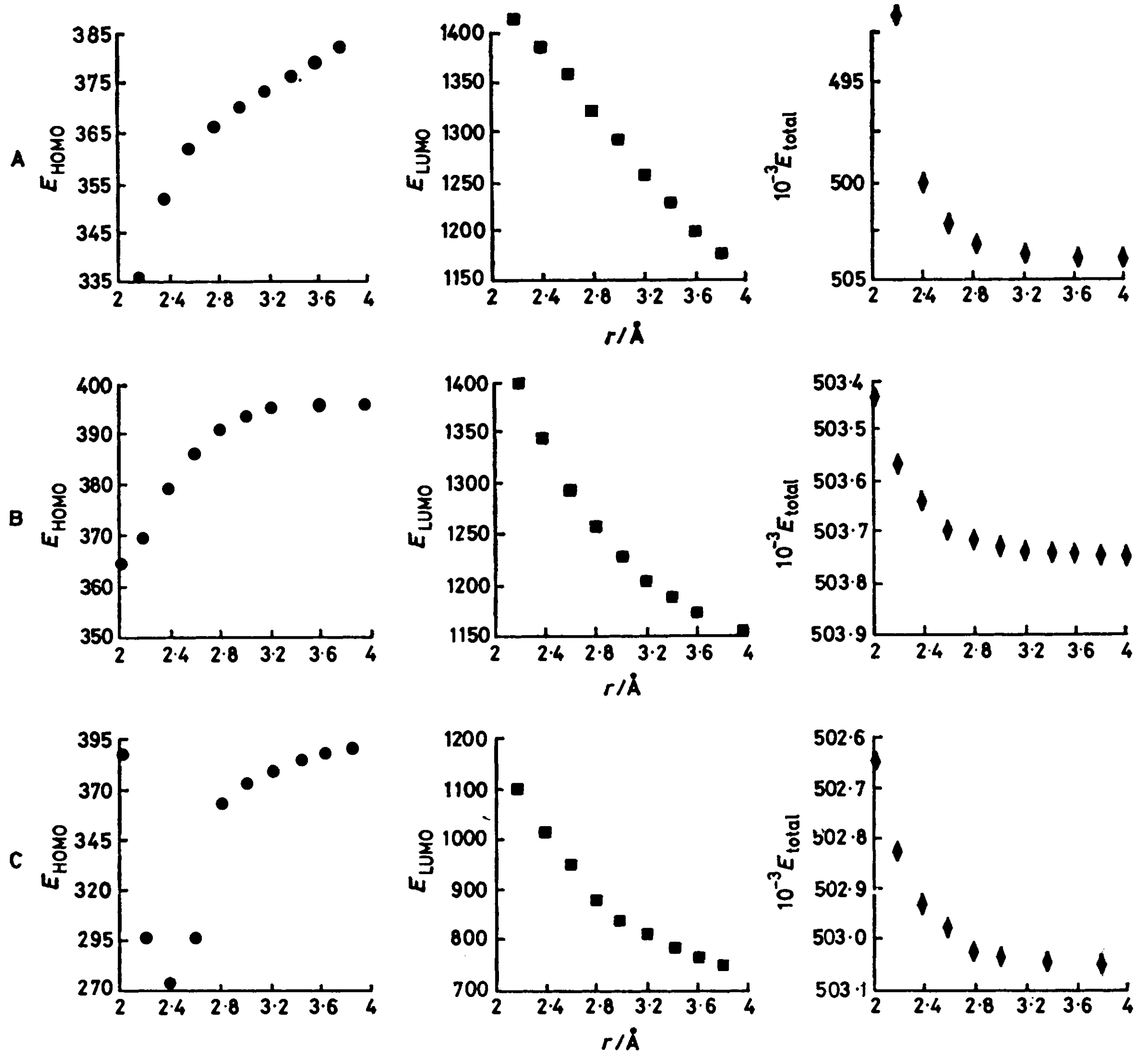


FIGURE 1 Total energy and frontier-orbital energy in kJ mol^{-1} *versus* fragment separation for allylic anion–ethylene interactions. A, B, and C respectively refer to approach of the allyl anion so that the dihedral angle between the C-1–C-2–C-3 plane and the atomic plane of ethylene is 0, 30, and 90° as indicated

(2) are again apparent. Even at the *ab initio* level, the two highest occupied levels of (2) are antibonding.

Charge distributions in (2) were obtained using the sphere-charge technique of Dean and Richards,[18] recently extended by Richards and Wallis.[19] This method effects a physically meaningful partition of the charge in the molecule and is not subject [20] to the defects of the Milliken population analysis, the usual method of charge partition. In particular, the results obtained are invariant to changes in the basis set. The charges within spheres centred on the carbon nuclei of (2) are shown in the Table. The radii of the spheres are equal to half the C-6–C-7 or C-2–C-3 internuclear distance, as appropriate. The values in the Table compare with 4.0204 electrons in an analogous sphere surrounding a carbon atom in ethylene, and 4.1082 and 3.9889 electrons for the terminal and central carbon atoms respectively in the allyl anion. We believe that the considerable increase for the carbon atoms of the ethylenic fragment of (2) and decrease for the terminal allylic carbons, compared with these reference values, is evidence for substantial homoconjugative delocalisation.

Electronic charges within spheres central on the carbon atoms in (2)

Atom	Radius of sphere (Å)	Charge in sphere (electrons)
C-2	0.698	4.0252
C-3	0.698	4.0370
C-4	0.698	4.0252
C-6	0.678	4.1040
C-7	0.678	4.1040

The sum over all spheres gives 20.2954 electrons for (2) and 20.2461 electrons for the reference species. This discrepancy accounts for only *ca.* 0.01 electrons per atom, and is too small to affect any conclusions drawn. Furthermore the MNDO-optimised carbon–carbon bond lengths for ethylene and allyl anion are, respectively, 1.335 and 1.380 Å. A reduction in bond order for both fragments therefore occurs in (2), which would be expected if there were partial bonding between C-4 and C-6 (and between C-2 and C-7).

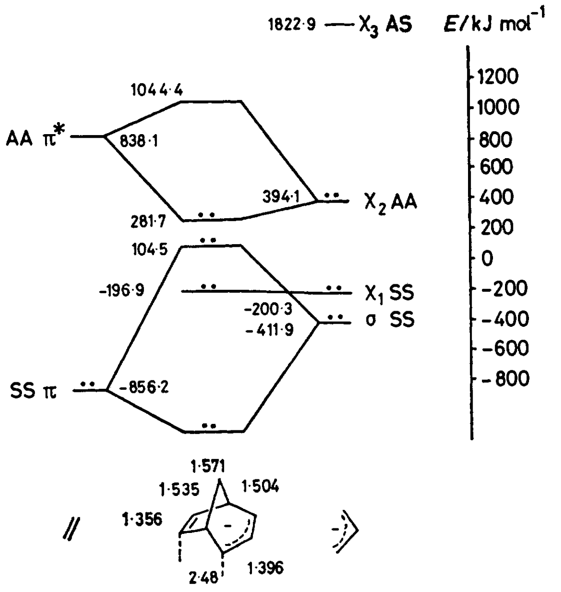


FIGURE 2 Comparison of the orbital energies of bicyclo-[3.2.1]octadienylide with those of allyl anion and ethylene

In conclusion we reassert an opinion that the stabilisation of (2) and (3) is primarily electronic. Earlier ideas on its detailed origin are doubtless naive, since arguments based solely on HOMO–LUMO interaction are not tenable. The energy changes in these orbitals consequent to allylic anion–olefin interaction are however in the expected sense.

[1/1281 *Received*, 11*th August*, 1981]

REFERENCES

[1] J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 1965, 376; J. M. Brown, *ibid.*, 1967, 638; S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Am. Chem. Soc.*, 1967, **89**, 3656.

[2] M. J. Goldstein, *J. Am. Chem. Soc.*, 1967, **89**, 6357; J. B. Grutzner and S. Winstein *ibid.*, 1972, **94**, 2200; M. V. Moncur and J. B. Grutzner, *ibid.*, 1973, **95**, 6449; M. J. Goldstein and S. Natowsky, *ibid.*, p. 6450.

[3] S. Winstein, *J. Am. Chem. Soc.*, 1959, **81**, 6524.

[4] G. B. Trimitsis and A. Tuncay, *J. Am. Chem. Soc.*, 1975, **97**, 7193; 1976, **98**, 1997.

[5] P. K. Freeman and T. A. Hardy, *Tetrahedron Lett.*, 1971, 3939.

[6] L. A. Paquette, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 106; L. A. Paquette, H. C. Berk, C. R. Degenhardt, and G. D. Ewing, *J. Am. Chem. Soc.*, 1977, **99**, 4764.

[7] A. J. Birch, A. L. Hinde, and L. Radom, *J. Am. Chem. Soc.*, 1980, **102**, 6430.

[8] P. H. Mazzochi, B. Stakly, J. Dodd, N. G. Rondan, L. N. Domelsmith, M. D. Rozebolm, P. Caramella, and K. N. Houk, *J. Am. Chem. Soc.*, 1980, **102**, 6482, and references therein.

[9] L. A. Paquette, R. A. Snow, J. L. Muthard, and T. Cynkowski, *J. Am. Chem. Soc.*, 1979, **101**, 6991.

[10] R. Sustmann and R. W. Gellert, *Chem. Ber.*, 1978, **111**, 42.

[11] E. Kaufman, H. Mayr, J. Chandrasekhar, and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1981, **103**, 1375.

[12] J. B. Gutzner and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1981, **103**, 1372.

[13] W. L. Jorgensen, *J. Am. Chem. Soc.*, 1976, **98**, 6784.

[14] J. Hine 'Structural Effects on Equilibria in Organic Chemistry,' Wiley, Chichester and New York, 1975, pp. 89ff; but see the recent discussion by D. F. de Tar, *J. Am. Chem. Soc.*, 1980, **102**, 7988.

[15] J. M. Brown, *J. Chem. Soc. B*, 1969, 868.

[16] S. W. Staley and D. W. Reichard, *J. Am. Chem. Soc.*, 1969, **91**, 3998.

[17] J. S. Binkley, R. A. Whitehead, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Henre, and M. D. Newton, *QCPE*, 1978, **11**, 368.

[18] S. M. Dean and W. G. Richards, *Nature*, 1975, **258**, 133.

[19] W. G. Richards and J. Wallis, *Proc. R. Soc. London, Ser. B*, 1977, 199, 291; J. Wallis, *QCPE*, 1981, **13**, 411.

[20] A. F. Marchington, S. C. R. Moore, and W. G. Richards, *J. Am. Chem. Soc.*, 1979, **101**, 5529.