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Π delocalisation in 1,3-butadiene: a nonempirical molecular orbital study

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Abstract. A value of −0.33 eV or −7.6 kcal mol^{-1} has been obtained for the vertical delocalisation energy of *trans*-1,3-butadiene from a nonempirical molecular orbital calculation on the π system. The result agrees well enough with ab initio calculations to suggest that a simplified approach need not be semiempirical. In a basis of orthogonalised atomic orbitals the central bond order is found to be 0.295 (Hückel value 0.447) for the delocalised structure and 0.125 for the localised (Hückel value zero). Core resonance integrals between neighbouring atoms, the analogues of Hückel's β, have theoretical values of −3.9 and −3.2 eV compared with −3.6 eV in benzene.

Key words: Delocalisation energy – Nonempirical molecular orbital theory – Theoretical core resonance integrals – Bond orders

1 Introduction

The determination of the vertical delocalisation energies (DEs) of benzene and 1,3-butadiene was achieved by ab initio methods 2 decades ago [1]. By contrast, qualitative understanding of π delocalisation and comparative ideas about aromaticity are still strongly influenced by the Hückel method [2] which, with all its faults, remains part of the education of every chemist. It seems surprising that there has not been more interest in correcting Hückel theory nonempirically, so that a simple explanatory theory of π delocalisation might have a well-defined quantum-mechanical model. Such an approach would have a different aim from the more usual semiempirical approach, where the aim is to achieve a good correlation with experimental data. DEs are not, in any case, well-defined experimental quantities.

An algebraic framework for improved π theories was established over 4 decades ago by Pople [3]; however, Pople's implementation of the formalism was semiempirical, and it retained two features of the Hückel scheme which obscured the underlying model: the neglect of overlap integrals and the parameterisation of the core resonance integral, β. It was soon realised [4] that using a basis of orthogonalised atomic orbitals (OAOs) would justify rigorously the neglect of overlap integrals and would justify approximately the neglect of those π-electronic repulsion integrals which involved overlap charge distributions [the zero differential overlap (ZDO) approximation]. It was also known that an explicit form for the core Hamiltonian could be derived from all-electron self-consistent-field (SCF) theory. This might have led to theoretical values of the core matrix elements, H^{c}_{pq}, and to a nonempirical treatment of π systems. Instead, the methodology of simplified calculations took the opposite course, extending the semiempirical approach to all the valence electrons [5].

In a recent nonempirical study of the π system in benzene [6] the present author used the all-electron linear combination of atomic orbitals (LCAO) SCF calculations of Buenker and Whitten [7] to infer theoretical values for β (which is really $H^{c}_{12} - H^{c}_{14}$ in this case) and for the repulsion integrals γ_{12} and γ_{14}, all in a basis of OAOs. These are the only integrals required to calculate the DE within the ZDO approximation. The value of the DE (−3.58 eV) was obtained by subtracting the total π energy of 1,3,5-cyclohexatriene from that of benzene, and this value was found to be in excellent agreement with both the ab initio SCF value (−3.68 eV) and the empirical value (−3.40 eV) used by Pople. Evidently simplified molecular orbital (MO) theory can give an acceptable DE without the use of parameters.

The theoretical value of β (−3.37 eV) is, however, very different from the semi-empirical value (−2.14 eV), because the bond orders used in the two approaches are different. For benzene itself the same (Hückel) bond orders are obtained whether one uses an OAO basis or simply normalises the MOs without overlap. For 1,3,5-cyclohexatriene, however, describing the two-centre MOs in terms of a full set of OAOs leads to small bond orders (about 0.1) between nonbonded adjacent atoms, where Hückel bond orders are zero. Hückel bond orders for the localised structure could have been obtained if each MO had been built from just two OAOs.

This procedure exactly reproduces Pople's algebraic expression for the DE, but it exaggerates the magnitude of the DE by a factor of 1.8 if theoretical integrals are used.

The benzene study shows how the Hückel account of delocalisation could be made theoretically sound, at least in a case where the AO combinations are determined by symmetry. Firstly, the localised structure should have the same σ framework as the actual molecule (i.e. it should not be an *n*-ethene system). Secondly, the bond orders should be determined in an explicit OAO basis. This is a useful result, for it means that the textbook account of the Hückel treatment of cyclic polyenes can be corrected without making it too complicated. Repulsion between the π electrons makes only a small contribution (about 10%) to the DE in benzene, and has no effect on the π-bond orders. To construct a more general improved theory it is obviously necessary to look at a π system where π-electronic repulsion does affect the bond orders. The simplest example is 1,3-butadiene.

2 Wavefunctions and energy integrals

LCAO SCF wavefunctions for *trans*-1,3-butadiene have been provided by Buenker and Whitten [8] using the same (10*s*, 5*s*/5*p*) G-lobe basis as in the benzene work. These MOs appear to be the best variational wavefunctions in which each $2p\pi$ AO is treated as a fixed group of functions, and for which the electronic spectrum has been calculated at the one-configuration level. The wavefunctions refer to an old experimental geometry [9] with an (assumed) ethene-like length (1.337 Å) for the terminal CC bonds and a value of 1.483 Å for the central bond. A later r_g geometry [10] has CC lengths at 1.344 and 1.467 Å, and this probably gives a truer picture of the effects of delocalisation upon geometry; however, the older geometry is adequate for the methodological purposes of the present calculations.

Using the LCAO coefficients of Buenker and Whitten and the orthonormality of the MOs, it is possible to deduce the (four) overlap integrals between the AOs (the ϕ basis) and then to use the full $\mathbf{S}$ matrix to form the OAO basis (χ) in the usual way:

$$\chi = \phi \mathbf{S}^{-1/2} \ . \tag{1}$$

The four MOs in the OAO basis are then given by

$$\psi_1 = 0.4203\chi_1 + 0.5686\chi_2 + 0.5686\chi_3 + 0.4203\chi_4 \tag{2}$$

$$\psi_2 = 0.5696\chi_1 + 0.4190\chi_2 - 0.4190\chi_3 - 0.5696\chi_4 \tag{3}$$

$$\psi_3 = 0.5686\chi_1 - 0.4206\chi_2 - 0.4206\chi_3 + 0.5686\chi_4 \tag{4}$$

$$\psi_4 = 0.4193\chi_1 - 0.5694\chi_2 + 0.5694\chi_3 - 0.4193\chi_4 \tag{5}$$

i.e. $\psi = \chi \mathbf{C}$.

The above coefficients do not conform precisely to the familiar pattern of Hückel MOs. Within pairs of MOs of the same symmetry (ψ_1 and ψ_3, or ψ_2 and ψ_4) the ratio C_1/C_2 in the one MO should be the same as $-C_2/C_1$ in the other; any deviation is a rounding error. However, within pairs of different symmetry (ψ_1 and ψ_2, or ψ_3 and ψ_4) the ratio C_1/C_2 is not quite the same as C_2/C_1 because the Fock matrix does not fulfil the requirements of an alternant hydrocarbon [11], when determined ab initio. In sect. 3, when bond orders are calculated, the coefficients in ψ_1 and ψ_2 will in effect be averaged so that C_1/C_2 is 0.4196/0.5691 in ψ_1 and 0.5691/0.4196 in ψ_2. For the moment, however, the above coefficients are the ones which will be used to determine the energy integrals.

The Fock matrix in the χ basis is now reconstituted from the diagonal matrix, ε, of published orbital energies:

$$\mathbf{F} = \mathbf{C}\varepsilon\mathbf{C}^{\dagger} \tag{6}$$

Off-diagonal elements of $\mathbf{F}$ are shown in Table 1.

The next step is to use the (theoretical) electronic spectrum to determine the Coulomb repulsion integrals, γ_{pq}, between OAOs. At the one-configuration level, the average of the triplet and singlet excitation energies arising from the excitation $\psi_i \rightarrow \psi_j$ is given by $\Delta E_{i\rightarrow j}$, where

$$\Delta E_{i\rightarrow j} - (\varepsilon_j - \varepsilon_i) = -J_{ij} + K_{ij} \ . \tag{7}$$

Values for the left-hand side of Eq. (7) have been given by Buenker and Whitten for the four excitations from ground-state MOs (ψ_1 and ψ_2) to the virtual MOs (ψ_3 and ψ_4). The (molecular) Coulomb and exchange integrals on the right-hand side of Eq. (7) may be expanded in terms of atomic integrals, γ_{pq}, using the ZDO approximation. Four equations are obtained in this way, with four unknowns:

$$\Delta E_{1\rightarrow 3} - (\varepsilon_3 - \varepsilon_1) = -6.980 = -0.5000\ (\gamma_{13} + \gamma_{12}) \tag{8}$$

$$\Delta E_{1\rightarrow 4} - (\varepsilon_4 - \varepsilon_1) = -7.880 = -\ 0.4565\ \gamma_{12} - 0.1242\ \gamma_{14} - 0.4194\ \gamma_{23} \tag{9}$$

$$\Delta E_{2\rightarrow 3} - (\varepsilon_3 - \varepsilon_2) = -6.587 = -\ 0.4565\ \gamma_{12} - 0.4194\ \gamma_{14} - 0.1242\ \gamma_{23} \tag{10}$$

$$\Delta E_{2\rightarrow 4} - (\varepsilon_4 - \varepsilon_2) = -7.156 = -0.5000\ (\gamma_{13} + \gamma_{12}) \ . \tag{11}$$

There is clearly an inconsistency between Eqs. (8) and (11) which arises from the neglect of polycentric integrals in the ZDO approximation. An average value (−7.068 eV) was taken of the left-hand sides, leaving three equations and

Table 1. Matrix elements

pq	12	13	14	23
S_{pq}	0.3440	0.0722	0.0091	0.2865
F_{pq}/eV	−8.09	0.235	0.631	−4.37
γ_{pq}/eV	8.79	5.34	3.73	8.11
H^{c}_{pq}/eV	−3.89	0.233	0.080	−3.17
R_{pq}	0.4777	0	−0.1477	0.1477
R^{loc}_{pq}	0.4961	0	−0.0624	0.0624

four unknowns. To reduce the number of unknowns, γ_{14} was approximated by an inverse-distance formula similar to the one proposed by Parr [15], originally for γ integrals between nonorthogonal AOs.

$$\gamma_{14} = (14.399/r_{14})\{1/2 + 1/2[1 + (r_p/r_{14})^2]^{-1/2}\} \tag{12}$$

The formula should be valid for OAOs provided the internuclear distance is very large (r_{14} = 3.687 Å in butadiene). The parameter r_p was calculated to be 1.672 Å by the requirement that Eq. (12) should reproduce the value (4.81 eV) of γ_{14} in benzene at the appropriate internuclear distance. On solving the (reduced) set of equations (Eqs. 8–12) one finds the values of the γ integrals displayed in Table 1. It is interesting and reassuring that the inverse-distance formula underestimates the values of γ_{13}, γ_{23} and γ_{12} by only 0.01, 0.03 and 0.04 eV, respectively, compared with the values in Table 1, which were obtained from the theoretical energy levels.

The final step is the calculation of the off-diagonal core matrix elements from the Fock matrix elements. In the ZDO approximation, the required relation is

$$F_{pq} = H^\mathrm{c}_{pq} - R_{pq}\,\gamma_{pq} \qquad (q \neq p) \tag{13}$$

$$\text{where} \quad R_{pq} = \sum_{i=1,2} C_{pi}\,C_{qi} \tag{14}$$

Values of the near-neighbour core integrals, H^c_{12} and H^c_{23}, (see Table 1) are very reasonable compared with a value of −3.60 eV for H^c_{12} in benzene, which was determined in a similar way from previous work [6]. The values of H^c_{13} and H^c_{14} are small and positive.

3 Bond orders and the calculation of the DE

Although butadiene is an alternant hydrocarbon [11] the π-bond orders between alternate atoms are not quite zero, and the atom charges are not quite unity, when the MOs have been determined by ab initio methods. The reasons for this were given in sect. 2. Using Eq. (14) together with Eqs. (2) and (3) to calculate the **R** matrix (which is half the charge and bond-order matrix, **P**) one finds that $R_{13} = R_{24} = 0.0030$, $R_{11} = 0.5010$ and $R_{22} = 0.4989$.

In order to retain the simplicity of the Hückel and Pople schemes and to exclude diagonal matrix elements from the calculation of the DE, values of R_{13} and R_{24} were set equal to zero and the diagonal elements were set equal to 0.5000. The **R** matrix obtained thereby is rigorously idempotent ($\mathbf{R}^2 = \mathbf{R}$) and refers to normalised MOs which differ only slightly from ψ_1 and ψ_2. Off-diagonal elements of **R** are shown in Table 1.

MOs for the localised structure are simply ethene-like combinations of the original AOs, suitably orthogonalised:

$$\psi_{12} \sim (\phi_1 + \phi_2) - \lambda\,(\phi_3 + \phi_4)$$

$$\psi_{34} \sim (\phi_3 + \phi_4) - \lambda\,(\phi_1 + \phi_2)\ .$$

It is found that λ is 0.0824. When the above MOs are normalised and transformed to the χ basis they have the form

$$\psi_{12} = 0.7125\chi_1 + 0.6989\chi_2 + 0.0446\chi_3 - 0.0437\chi_4$$

$$\psi_{34} = -0.0437\chi_1 + 0.0446\chi_2 + 0.6989\chi_3 + 0.7125\chi_4\ . \tag{15}$$

The $\mathbf{R}^\mathrm{loc}$ matrix obtained from these coefficients does not quite have an alternant structure, but can be made so by small adjustments which preserve idempotency. Values of R^loc_{11} and R^loc_{44} have to be reduced by 0.0095, while R^loc_{22} and R^loc_{33} must be increased by the same amount, in order to obtain 0.5000 for all diagonal elements. Bond orders between alternate atoms which were 0.0012 are set equal to zero. The values of R^loc_{12}, R^loc_{14} and R^loc_{23} are shown in Table 1.

All the information is now available for the calculation of DE. The general expression for the energy of a π system (in the ZDO approximation) is given by

$$E = \sum_p \sum_{q \neq p} (2H^\mathrm{c}_{pq}\,R_{pq} - \gamma_{pq}\,R^2_{pq}) + \sum_p W_p\ , \tag{16}$$

where W_p is given by

$$W_p = H^\mathrm{c}_{pp} + 1/4\,\gamma_{pp} + \sum_{q \neq p} 1/2\gamma_{pq} \tag{17}$$

for all alternants (R_pp = 0.5000), and is the same for both the delocalised and localised π systems. The total energy of the localised system, E^loc, is found from Eq. (16) by substituting elements of R^loc for those of R. Upon subtracting E^loc from E, diagonal terms, W_p, vanish:

$$\begin{aligned} \mathrm{DE} &= E - E^\mathrm{loc} \\ &= 8\,H^\mathrm{c}_{12}(R_{12} - R^\mathrm{loc}_{12}) + 4(R_{23} - R^\mathrm{loc}_{23})\,(H^\mathrm{c}_{23} - H^\mathrm{c}_{14}) \\ &\quad - 4\,\gamma_{12}(R^2_{12} - R^\mathrm{loc}_{12}\,R^\mathrm{loc}_{12}) - 2(R^2_{23} - R^\mathrm{loc}_{23}\,R^\mathrm{loc}_{23}) \\ &\quad \times (\gamma_{23} + \gamma_{14})\ . \end{aligned} \tag{18}$$

A simplification has been achieved as a consequence of the equalities

$$R_{23} = -R_{14} \quad \text{and} \quad R^\mathrm{loc}_{23} = -R^\mathrm{loc}_{14}\ ,$$

and a further simplification could follow from

$$R^2_{12} - R^\mathrm{loc}_{12}\,R^\mathrm{loc}_{12} = R^2_{23} - R^\mathrm{loc}_{23}\,R^\mathrm{loc}_{23}\ .$$

However, substituting appropriate values from Table 1 into Eq. (18) gives

$$\mathrm{DE} = -0.33\,\mathrm{eV} \text{ or } -7.6\ \mathrm{kcal\ mol^{-1}}$$

4 Discussion

The above value of the DE agrees quite well with the value (−9.5 kcal mol^{-1}) obtained by Kollmar [1] in ab initio SCF calculations using a double zeta basis. It also agrees more closely with his value including correlation (−8.4 kcal mol^{-1}). As in the benzene case, neglecting polycentric repulsion integrals has made the localised structure relatively more stable; however, the effects of this approximation, together with the effects of forcing the **R** matrices to have alternant structure, do not seem to have been too detrimental. Simple MO theory has given a qualitatively correct account of the DE without adjustable parameters.

The contribution of π-electronic repulsion to the DE is 0.206 eV or 4.75 kcal mol^{-1}, as compared with 12.4 kcal mol^{-1} for a similar calculation in benzene. However, in butadiene the contribution of π-electronic repulsion cancels out 38% of the one-electron contribution, compared with 13% in benzene.

An indication of the extent of delocalisation in butadiene can be gained from the difference between the central bond order in the delocalised structure and that in the localised one. One finds that $P_{23} = 0.2954$ and $P_{23}^{\text{loc}} = 0.1248$, the corresponding Hückel values being 0.4472 and zero respectively. It has long been realised that Hückel theory with equal β values for the bond integrals overestimates P_{23} compared with the SCF value. Less well known is the fact that Hückel theory underestimates P_{23}^{loc} compared with its value in an OAO basis. The importance of being explicit about the nature of the basis set when comparing bond orders was not fully appreciated in the historic controversy between Dewar [12] and Mulliken [13] about the extent of delocalisation in butadiene.

The use of Hückel bond orders (i.e. $R_{12}^{\text{loc}} = 0.5000$ and $R_{23}^{\text{loc}} = 0.0000$) for the localised structure together with correct values of R_{12} and R_{23} for the delocalised system leads, via Eq. (18), to a DE value of −22.5 eV, or about 3 times the value obtained in Sect. 3. A similar exercise in benzene multiplies the value of the DE by a factor of 1.8. The disparity between these factors underlines the difficulty, in a semiempirical treatment, of finding parameters which will compensate for incorrect bond orders.

A general nonempirical MO theory of π systems will require some simple algorithms for calculating the β and γ integrals. The approximate SCF calculation of bond orders could then be carried out independently of ab initio results. For the γ integral, the values in Table 1 could be fitted to a simple power series in $1/r$ where r is the internuclear distance. The case of the β integrals is more complicated. A common assumption in many simplified schemes is that a β integral between neighbouring OAOs is proportional to the overlap integral between AOs, and that β integrals between nonneighbours are negligible. So far as the author is aware, there has never been a numerical justification for these assumptions based on all-electron calculations, although there has been some algebraic justification [14]. Table 1 provides some numerical evidence. One finds that

$$-H_{12}^{\text{c}}/S_{12} = 11.3 \text{ eV} \quad \text{and} \quad -H_{23}^{\text{c}}/S_{23} = 11.1 \text{ eV} .$$

To the above may be added a result from the benzene calculation, where $-\text{H}_{12}^{\text{c}} = 3.60$ eV, $\text{S}_{12} = 0.3220$ and the ratio is 11.2 eV. It seems that for the AO basis used in the present work an appropriate relation for near-neighbour resonance integrals is

$$\beta = -11.2S$$

provided that the distance between neighbours is in the range 1.33–1.49 Å.

So far as nonneighbour resonance integrals are concerned, H_{13}^{c} is not negligible in butadiene; however, it will be multiplied by a zero element of **R**, and this will be the case in other alternants. Neglecting H_{14}^{c} in butadiene decreases the magnitude of the DE by 1.26 kcal mol^{-1} or 16%. A similar approximation in benzene, where H_{14}^{c} is −0.235 eV, increases the magnitude of the DE by 6.6 kcal mol^{-1} or 8%. It is interesting that H_{14}^{c} is negative in the cyclic molecule and positive for the open chain; however, there does not seem to be an easy way of estimating either the value of H_{14}^{c} or the effect of neglecting it, in general.

References

1. Kollmar H (1979) J Am Chem Soc 101: 4832
2. Hückel E (1931) Z Phys 70: 204
3. Pople JA (1953) Trans Faraday Soc 49: 1375
4. Löwdin P-O (1955) Sven Kem Tidskr 67: 380
5. Pople JA, Beveridge DL (1970) Approximate molecular orbital theory. McGraw-Hill, New York
6. Melrose MP (1997) Theor Chim Acta 95: 67
7. Buenker RJ, Whitten JL, Petke JD (1968) J Chem Phys 49: 2261
8. Buenker RJ, Whitten JL (1968) J Chem Phys 49: 5381
9. Almenningen A, Bastiansen O, Traetteberg M (1958) Acta Chem Scand 12: 1221
10. Haugen W, Traetteberg M (1966) Acta Chem Scand 20: 1726
11. Parr RG (1963) Quantum theory of molecular structure. Benjamin, Reading, Mass. p 79
12. Dewar MJS, Schmeising HN (1960) Tetrahedron 11: 96
13. Mulliken RS (1959) Tetrahedron 6: 68
14. Fischer-Hjalmars I (1965) Adv Quantum Chem 2: 55
15. Parr RG (1952) J Chem Phys 20: 239