474. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part IX.* Hexatomic Molecules: Ethylene.*

By A. D. Walsh.

The electronic orbitals of the ethylene molecule are described. It is concluded that the first, triplet or singlet, excited state of the molecule should have (i) a pyramidal arrangement of the bonds about each C atom, (ii) one CH_2 group twisted relative to the other through 90° about the C–C bond, and (iii) each C atom possibly slightly out of the mirror plane that bisects the HCH angle of the other CH_2 group. The first excited state of a molecule containing n electrons should belong to the same symmetry class as the ground state of a similar molecule containing $n + 1$ or $n + 2$ electrons. The symmetry of the ground state of the N_2H_4 molecule affords strong support for conclusions (i) and (ii) concerning the first excited state of the C_2H_4 molecule.

Orbitals of C_2H_4.—The ethylene molecule in its ground state belongs to the symmetry class V_h. The definitions of the symbols appropriate to the orbitals of such a molecule are given in the Table below. yz is taken as the plane of the molecule, z being the long axis. $C_2(z)$ and $C_2(y)$ denote rotations of 180° about the z and the y axis respectively. $\sigma_\iota(z)$ and $\sigma_V(y)$ denote reflections in planes perpendicular to the z and the y axis respectively. i denotes the operation of inversion at the centre of symmetry.

Each CH_2 group, in symbols appropriate to its localized C_{2v} symmetry, will contain orbitals a_1, b_2 as for HCHO (see Part VI). Orbital a_1, having fewer nodal surfaces, is the more tightly bound. Considering non-localised orbitals, we obtain from the two a_1 orbitals new orbitals—one a sum and the other a difference. The new orbitals extend over the whole molecule and it is therefore appropriate to describe them by symbols of the V_h group. The first is bonding between the two CH_2 groups and is a_{1g} in type; the second is anti-bonding between the two CH_2 groups and is b_{1u} in type; both are bonding in all the C–H links.

Symbols used for molecular orbitals of V_h *molecules.*

Symbol	$C_2(z)$	$C_2(y)$	$\sigma_V(y)$	$\sigma_V(z)$	i	Symbol	$C_2(z)$	$C_2(y)$	$\sigma_V(y)$	$\sigma_V(z)$	i
a_{1g}	+	+	+	+	+	b_{2g}	−	+	+	−	+
a_{1u}	+	+	−	−	−	b_{2u}	−	+	−	+	−
b_{1g}	+	−	−	+	+	b_{3g}	−	−	−	−	+
b_{1u}	+	−	+	−	−	b_{3u}	−	−	+	+	−

Fig. 1 shows the forms of the two b_2 orbitals. They give one non-localized orbital that is bonding between H_1 and H_3, H_2 and H_4, and another that is anti-bonding between H_1 and H_3, H_2 and H_4. Both are anti-bonding from H_1 to H_2 and from H_3 to H_4. The first is b_{2u} and the second b_{3g}. With respect to the symmetry of the whole molecule, the orbitals that are often loosely referred to as the "σ" and "π" orbitals of the C–C bond possess the labels a_{1g} and b_{3u} respectively. More explicitly, they might be symbolized $[C(\text{hybrid})_z + C(\text{hybrid})_z], a_{1g}$ and $[C(2p_x) + C(2p_x)], b_{3u}$ respectively. The whole ground-state configuration of the C_2H_4 molecule may therefore be written

$$(a_{1g})^2(b_{1u})^2(a_{1g})^2(b_{2u})^2(b_{3g})^2(b_{3u})^2,\ {}^1A_{1g}$$

There is general agreement that the (b_{3u}) or "π" orbital is the most weakly bound orbital to be occupied in the ground state. An anti-bonding "π" orbital is also possible. It may be symbolized as $[C(2p)_x - C(2p)_x), b_{2g}$. Just as we have seen (Part VI) that the experimental facts fit with the anti-bonding "π" orbital's being the lowest orbital unoccupied in the ground state of CH_2O, so we may expect the corresponding orbital to be the lowest orbital unoccupied in the ground state of C_2H_4.

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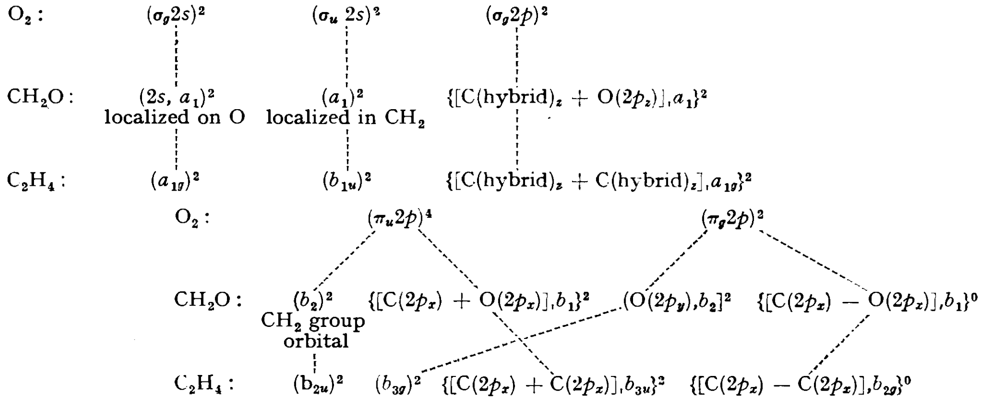
* Part VIII, preceding paper.

It will be useful to formulate the symbols for corresponding orbitals of the isoelectronic O_2, CH_2O, and C_2H_4 molecules :



It will be seen that the degeneracies of the $(\pi_u 2p)$ and $(\pi_g 2p)$ orbitals are split in passing from O_2 to CH_2O. The indices refer to the number of electrons occupying the orbitals in the ground states. The energy order of the orbitals for O_2 is established. It is likely that the corresponding order is maintained in CH_2O and C_2H_4, except for the reversal of the two outermost orbitals occupied in the ground states of CH_2O and C_2H_4. This reversal is understandable in terms given below.

Just as we showed in Part VI that the anti-bonding " π " orbital in CH_2O had maximum binding energy when the HCH angle ($\doteqdot$ the HCO angle) was 90°, so it can be shown that the corresponding orbital in C_2H_4 has maximum binding energy when the HCH($\doteqdot$ the HCC angle) is 90°. It is sufficient to base our expectation, however, on the correspondence of the orbitals between the two isoelectronic molecules, and to conclude that the C_2H_4 transition

$$\cdots (b_{3u})(b_{2g}),\ {}^1B_{1u} \longleftarrow \cdots (b_{3u})^2,\ {}^1A_{1g} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

leads to an upper state that has a pyramidal arrangement of the bonds about each C atom. It is also possible (cf. CH_2O) that in the excited state each C atom will lie slightly out of the mirror plane of the other CH_2 group that is perpendicular to the plane of that CH_2 group.* These conclusions have not previously been realized. (1) is probably the lowest-energy singlet–singlet transition of the molecule.†

This does not suffice, however, to determine the shape of the excited C_2H_4 molecule. A further change of shape is possible with C_2H_4 that was impossible with CH_2O, namely, a twisting of the two CH_2 groups relative to each other about the C–C bond.

Twisting of the CH_2 *Groups about the* C–C *Bond.*—Consider first the O_2 molecule. The molecular-orbital explanation of why the ground state of the O_2 molecule is a triplet is simple and well-known. However, an equally simple explanation can be given as follows.‡ Suppose the molecule to be formed by the approach of two O atoms along the z direction. Suppose the configuration of each atom is

$$\cdots 2p_x\, 2p_y^2\, 2p_z$$

Then the $2p_z$ atomic orbitals overlap to form a σ bond, while the $2p_x$ atomic orbitals overlap to form a π bond. This means that, in addition, a $2p$ lone-pair of electrons is

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* The explanation would be that excitation of an electron from the b_{3u} CC orbital results in the b_{3g} CH_2 group orbital being " pulled " away from the H atoms and more on to the C atoms, and that an occupied orbital that is largely built from in-plane $2p$ orbitals on the C atoms tends to cause in-plane bending of the molecule.

† Craig (*Proc. Roy. Soc.*, 1950, *A*, **200**, 272), however, considers the first singlet–singlet transition to be ${}^1A_{1g} \longleftarrow {}^1A_{1g}$, where the upper state arises by a *two*-electron jump to the (b_{2g}) orbital. Moffitt (*Proc. Phys. Soc.*, 1950, **63**, *A*, 585) has criticized this.

‡ This explanation should be used with care, especially when it is remembered that there is no practical distinction between the x- and the y-direction for a linear molecule. Nevertheless, the author believes it to be of value in giving a very simple way of gaining some insight into the fundamental reasons for the triplet ground state of O_2 and the shape of the H_2O_2 molecule, their connection with the low height and twisted nature of the C_2H_4 lowest triplet state, and several facts concerning the CH_2O molecule.

present on each atom, these electrons being in orbitals pointing in the same direction. Lone pair–lone pair repulsion is thus present. The repulsion arises from four electrons trying to occupy the same orbital in the region of overlap. By the Pauli principle, they cannot do this. The difficulty can be avoided either by supposing that the two pairs of electrons repel each other, so that their orbitals do *not* overlap, or by constructing *two* new molecular orbitals (one bonding and one anti-bonding). The second alternative is adopted in the most usual orbital theory. The first is adopted here and its possibilities explored. Lone pair–lone pair repulsion is a language used, *e.g.*, by Walsh (*J.*, 1948, 398) to express an effect that, on more usual theory, would be described by saying that excitation of electrons to anti-bonding molecular orbitals occurs.

Of course, there is no actual distinction of the x and the y direction for a linear molecule, so that the proper wave functions would be combinations of those built as above and those in which the x and y suffixes were interchanged; but we can still conceive of a state of the O_2 molecule in which all electrons are paired and wherein occur

$$\text{A } \sigma \text{ bond} + \text{a } \pi \text{ bond} + \text{lone pair–lone pair repulsion} \quad . \; . \; . \quad (2)$$

The repulsion could be avoided if, as the two atoms approached, their configurations were supposed to be twisted with respect to each other so that one obtained

$$\text{A } \sigma \text{ bond} + \underbrace{\substack{\text{interaction of odd electron} \\ \text{and lone pair}}}_{\substack{\text{in orbitals ``pointing'' in} \\ \text{the } x \text{ direction}}} + \underbrace{\substack{\text{interaction of odd electron} \\ \text{and lone pair}}}_{\substack{\text{in orbitals ``pointing'' in} \\ \text{the } y \text{ direction}}} \quad . \; . \; . \; . \quad (3)$$

The latter two interactions could be called " three-electron bonds." There is empirical evidence that such interactions are attractive, with a strength about one-half of that of the corresponding single bond. Theoretically, this is most simply seen by reverting for a moment to the usual orbital language and noting that two electrons would occupy the bonding $\psi_1(2p) + \psi_2(2p)$ orbital and one the corresponding anti-bonding $\psi_1(2p) - \psi_2(2p)$ orbital, giving a net effect of approximately half a filled bonding orbital. Expression (3) may thus be re-written as

$$\text{A } \sigma \text{ bond} + \sim \tfrac{1}{2} \text{ a } \pi \text{ bond} + \sim \tfrac{1}{2} \text{ a } \pi \text{ bond}$$

or

$$\text{a } \sigma \text{ bond} + \sim \text{a } \pi \text{ bond} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

but without any repulsion effect. Comparing this with (2), one sees that it is probable that the state of the O_2 molecule reached by the second mode of interaction of two O atoms lies lower in energy than the state reached by the first mode of interaction. One can therefore understand why the ground state of the O_2 molecule should contain two unpaired electrons. The essential reason may be thought of as the twisting of one O atom configuration relatively to the other to eliminate the lone pair–lone pair repulsion that would otherwise be present.

Such an account at once explains why the ground state of the H_2O_2 molecule should be skew and not planar. One H atom pairs with the odd " $2p_x$ " electron and the other with the odd " $2p_y$ " electron of the O_2 ground state.

Consider now the C_2H_4 molecule. A CH_2 group is isoelectronic with an O atom and, as we have seen, the orbitals of C_2H_4 correspond to those of O_2. In particular, the b_2 CH_2 group orbitals correspond to the $2p\pi$ O orbitals of the O_2 molecule. The electrons in the filled b_2 CH_2 group orbitals must repel each other in the C–C bond of C_2H_4, just as the electrons in the filled, parallel, $2p\pi$ atomic orbitals repel each other in the O–O bond of singlet O_2. This repulsion is described in alternative language by saying that two electrons occupy the $CH_2 \longleftrightarrow CH_2$ anti-bonding (b_{3g}) molecular orbital. On the other hand, the repelling b_2 CH_2 group electrons are further apart (see Fig. 1) than would be repelling O $2p\pi$ electrons. The repulsion in the ground state of the C_2H_4 molecule, analogous to the lone pair–lone pair repulsion of the O_2 molecule, will therefore be comparatively weak and it is not surprising that the ground state of C_2H_4, unlike that of O_2, is singlet. The magnitude of the repulsion will be indicated by the energy needed to raise the C_2H_4

molecule to a triplet state analogous to O_2 $^3\Sigma_g^-$. Estimates of this energy vary, but there is general agreement that the C_2H_4 molecule does have a comparatively low-lying triplet state. The reason for the low height can be thought of as the tendency of the two CH_2 groups to twist relatively to each other in order to remove the analogue of the lone pair–lone pair repulsion existing in, for example, the O_2 $^1\Delta_g$ or $^1\Sigma_g^+$ state. In the ground state the tendency to twist is opposed by the tendency of the " π " C–C bond to keep the two CH_2 planes identical. In the upper state of transition (1), however, this opposition is partly removed, the effect of the anti-bonding (b_{2g}) electron roughly cancelling that of the bonding b_{3u} electron. One deduces that the excited state (other geometrical changes being for the moment neglected) will be most stable when the planes of the two CH_2 groups are at 90°.

Olson (*Trans. Faraday Soc.*, 1931, **27**, 69) first suggested that the C_2H_4 absorption near 2000 Å involved an upper state of this shape. The conclusion has been deduced theoretically, in language less simple than that used here, by Mulliken (*Rev. Mod. Phys.*, 1942, **14**, 265) and by Mulliken and Roothaan (*Chem. Reviews*, 1947, **41**, 219). Mulliken called the $CH_2 \longleftrightarrow CH_2$ repulsion that is responsible " second-order hyperconjugation."

The CH_2O molecule must be even closer than C_2H_4 to O_2 in electronic structure. The analogue of the lone pair–lone pair repulsion will now be between the electrons in the CH_2 b_2 group orbital and those in the $O(2p_y),b_2$ lone-pair orbital. It will be stronger than the corresponding repulsion in C_2H_4. Various consequences of this may be traced in the facts relating to the CH_2O molecule. For the present we note that it explains the reversal in the energy order of the two outermost orbitals occupied in the ground states of CH_2O and C_2H_4. Because the lone pair–lone pair repulsion, which makes the $(\pi_g 2p)$ orbital of O_2 and the corresponding $O(2p_y),b_2$ orbital of CH_2O lie high in energy, is much weaker in C_2H_4, the corresponding (b_{3g}) orbital of C_2H_4 will be more tightly bound relatively to the other C_2H_4 orbitals.

FIG. 1.

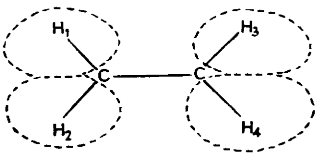
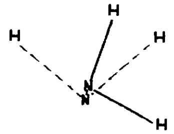


FIG. 2.



Shape of the First Excited State of C_2H_4 : *Evidence.*—The conclusion reached above is that in its first excited state (either singlet or triplet) the C_2H_4 molecule should have (i) one CH_2 group twisted though 90° relative to the other, (ii) a pyramidal arrangement of the bonds about each C atom, and (iii) each C atom possibly slightly out of the mirror plane bisecting the HCH angle of the other CH_2 group. That at least the first two of these conclusions are correct can be strongly supported as follows. A corollary of the molecular-orbital approach adopted in this series of papers is that the symmetry of the first excited state of a molecule containing n electrons should be the same as that of the ground state of the similar molecule containing $n + 1$ or $n + 2$ electrons. The latter, in relation to the ground state symmetry of the molecule containing n electrons, reveals how the first excited orbital of the latter tends to stabilize the molecule, a tendency possibly all the greater in the first excited state of the n-electron molecule because one electron may then be missing from an orbital tending to stabilize the molecule in its original shape. As examples of the corollary, the first excited state of CO_2 should belong to the same symmetry class as the ground states of NO_2 and SO_2; the first excited state of NO_3^- should have the same symmetry as the ground state of NF_3; and the first excited state of CH_2O should be similar to the ground state of H_2NF. We can therefore test our conclusions as to the symmetry of the first excited state of C_2H_4 by means of the shape of the ground state of the hydrazine molecule. Scott, Oliver, Gross, Hubbard, and Huffman (*J. Amer. Chem. Soc.*, 1949, **71**, 2293; see also Wagner and Bulgozdy, *J. Chem. Phys.*, 1951, **19**, 1210, and Giguère and Liu, *ibid.*, 1952, **20**, 136), from the evidence of infra-red spectroscopy concluded that the molecule has a pyramidal arrangement of the bonds about each N atom, a staggered configuration of the H atoms (somewhat as Fig. 2) being favoured. Collin and Lipscomb (*Acta Cryst.*, 1951, **4**, 10) suggest that in the crystal the H atoms lie in the opposed or eclipsed configuration. However, the barrier to rotation about the N–N bond should be small, so that crystal forces might cause the eclipsed form to be more stable in the solid state, even though the staggered configuration is the more stable in the isolated molecule. The configuration favoured by Scott *et al.* is just that expected for the first excited state of C_2H_4 on the basis of (i) and (ii) above. There appears to be no evidence to support expectation (iii), but the deviation may be so small as not to be easily detected.

Vibrational Structure to be expected for the First Transition of C_2H_4.—In the light of our expectations as to the shape of the $^1B_{1u}$ state of C_2H_4, at least the following vibrations might be expected to appear in the transition (1) or its triplet$\leftarrow$singlet analogue: (i) the C–C valence vibration, ν_2a_g, which has a frequency 1623 cm.$^{-1}$ in the ground state; (ii) the CH_2–CH_2 twisting vibration, ν_4a_u, which has a frequency 1027 cm.$^{-1}$ in the ground state (Arnett and Crawford, *J. Chem. Phys.*, 1950, **18**, 118); (iii) one or both of the out-of-plane bending vibrations, ν_7b_{1u} and ν_8b_{2g}, which have frequencies 949 and 943 cm.$^{-1}$ respectively in the ground state (these are included because of the tendency of the C atoms to assume a pyramidal bond arrangement); (iv) one or both of the in-plane deformation vibrations, $\nu_{10}b_{2u}$ and ν_6b_{1g}, which have frequencies 995 and 1050(?) cm.$^{-1}$ respectively in the ground state (these may be thought of as arising from the rotation of the two CH_2 groups about axes perpendicular to the molecular plane, and are included because of the expectation that each C atom may lie out of the mirror plane bisecting the HCH angle of the other CH_2 group). In addition, the following might also occur: (v) one or both of the CH_2 deformation vibrations ν_3 and ν_{12} which change the HCH angles relatively to the HCC angles [they are included because it is improbable that in the excited state angle HCH remains approximately equal to angle HCC (cf. Part VIII)]; (vi) one or both of the CH stretching vibrations ν_1 and ν_{11} (these are included because the change of bond arrangement from planar to pyramidal implies that the C valencies towards the H atoms, and hence the C–H stretching force constants change).

If, as is probable from the arguments above, the upper state departs appreciably from V_h symmetry, the symbol B_{1u} is not strictly applicable and any symmetry restrictions on which vibrations can occur are relaxed. Unfortunately, the absorption that is best identified as transition (1) is continuous, having a maximum at *ca.* 1615 Å. It is difficult therefore to test our expectations. A system of bands observed by Snow and Allsopp (*Trans. Faraday Soc.*, 1934, **30**, 93) in the range 1935—2069 Å and yielding a frequency between 760 and 920 cm.$^{-1}$ may either represent the tail of the 1615-Å absorption or the $^1A_{1g} \longleftarrow {}^1A_{1g}$ transition suggested by Craig or part of the triplet$\leftarrow$singlet analogue of (1) (Moffitt, *loc. cit.*). In the second of these possibilities the system is due to a two-electron jump between the same two orbitals as the one-electron jump (1). In any case, therefore, the frequencies involved are likely to represent one or more of the vibrations (i)—(iv).—The biggest changes of geometry in the equilibrium form of the upper state are probably the lengthening of, and twisting about, the C–C bond. Vibrations (i) and (ii) are perhaps therefore likely to be the most prominent. It is noteworthy that Reid (*J. Chem. Phys.*, 1950, **18**, 1299) has observed a system of weak absorption bands in the near ultra-violet which is plausibly supposed to represent the triplet–singlet analogue of (1), and has attributed the band separation of 995 cm.$^{-1}$ to the upper-state twisting frequency. It is also noteworthy that the first known absorption of *cyclo*pentene (Carr and Stuecklen, *ibid.*, 1938, **6**, 55) shows a long succession of narrow shallow bonds which have separations of 90—160 cm.$^{-1}$ and are believed to represent puckering vibrations of the ring, which are to be expected on the basis of expectations (i)—(iv) above.

The list of possible C_2H_4 vibrations that might appear in its spectrum is a formidable one and there is little direct evidence in favour of most of the possibilities. Nevertheless, indirect support for the ideas on which the list is based is to be found in the spectrum of benzene which is briefly dealt with in the following paper.

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