On the Planarity of Butatriene

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The two-dimensional Hückel molecular orbital theory is applied to butatriene, considering both the planar (D_{2h}) and twisted (D_{2d}) conformations. The planar structure is found to be the energetically more stable one for the normal molecule. This result is consistent with previous structural and spectroscopical investigations. The present analysis also suggests a less stable twisted C_4H_4 diradical. The ions $C_4H_4^{2-}$ and $C_4H_4^{2+}$ are found to be more stable in the twisted form. The hypothetical twisted butatriene explains several properties of C_4H_4, in particular its tendency to polymerize.

Molecules with unusual electronic configurations have for a long time fascinated organic chemists. Much of the present knowledge of the structures of reactive intermediates has stemmed from this interest. Butatriene, C_4H_4, is the smallest possible molecule with three cumulated double bonds. It was first synthesized by Schubert et al.[1] and later by Kloster-Jensen (described by Almenningen et al.[2]) and others,[3] following basically the same method.

The structure of butatriene in the gas phase has been investigated by high-resolution Raman spectroscopy[4] and electron diffraction.[2] These works concentrated on the determination of accurate CC bond distances. They did not prove directly the planarity of butatriene, but neither did they contradict a planar structure with a linear carbon skeleton.

A few infrared (IR) bands of butatriene were reported in connection with the synthesis of the molecule.[1] Another rudimentary IR spectrum appeared later.[5] Further IR bands were reported privately to one of the present authors[5] by D. F. Eggers, Jr., who suggested a partial experimental assignment of fundamentals. A more complete analysis with an assignment of IR fundamentals is due to Cyvin et al.[6] These authors[6] were aware of the difficulties of recording a Raman vibrational spectrum because of rapid polymerization of butatriene in the liquid phase. This difficult task was accomplished by Miller et al.,[3] who supplied an almost complete experimental assignment of the vibrational frequencies based on both IR and Raman spectra. These authors[3] considered in detail the expected spectral features for a planar structure (symmetry D_{2h}) and the twisted one (symmetry D_{2d}), where the two CH_2 groups are perpendicular to each other. They concluded with confidence that the symmetry of butatriene is D_{2h} rather than D_{2d}.

A few papers have appeared on the normal coordinate analysis of butatriene[7–10] with calculations of some molecular constants. In all cases the planar (D_{2h}) structure of the molecule is assumed.

In the present work the two-dimensional HMO (Hückel molecular orbital) theory[11] is applied to butatriene. Both of the planar (D_{2h}) and twisted (D_{2d}) structures are considered. The analysis suggests the possible existence of a butatriene radical with the twisted conformation.

APPLICATION OF THE TWO-DIMENSIONAL HMO THEORY

The σ binding system of the butatriene skeleton consists of two central sp-hybridized C atoms and two terminal C atoms with sp^2-hybridization. Hence there is one $2p$ orbital at each terminal C and two perpendicular ones at each central C atom available for the formation of the π system. The π-system molecular orbitals are formed as linear combinations at the $2p$ orbitals exactly as in the conventional HMO theory,[12] but taking into
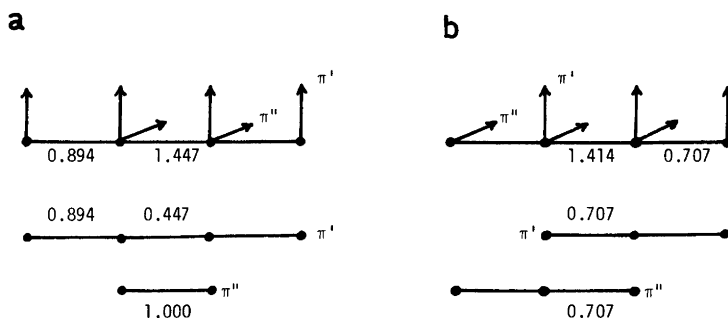
a   b

Fig. 1. The π systems of butatriene, (a) planar (D_{2h}) and (b) twisted (D_{2d}). The values of π bond orders are included.

account both directions perpendicular to each other. Thus two independent parts of the π system are constructed, say π' and π''. Fig. 1 shows schematically the $2p$ orbitals building up the π systems in the cases of (a) the planar (D_{2h}) and (b) twisted (D_{2d}) structures. In these two cases and within the simplest approximation of the HMO theory[12] the π' and π'' systems are found to be identical with (a) 1.3-butadiene (π') and ethylene (π''), and (b) two times allyl $(\pi'$ and $\pi'')$, respectively. These features are included in a symbolical way in Fig. 1.

The simple HMO treatment[12] of all the above-mentioned systems is well known. Fig. 2 shows the HMO energy levels in terms of the conventional constants α and β. The total π-system energy (E_π) is obtained according to the simplest approximation by adding up the contributions from each electron. The π-ground state electron configurations are indicated on Fig. 2. As a result of this analysis one obtains

(a) $E_\pi(\text{planar}) = 6\alpha + 6.472\beta$

(b) $E_\pi(\text{twisted}) = 6\alpha + 5.657\beta$

and consequently

$E_\pi(\text{planar}) < E_\pi(\text{twisted})$

As expected, the planar configuration is energetically more stable than the twisted one. The energy difference is about 0.82β.

The π bond orders were calculated in the usual way[12] with the results given in Fig. 1. The total π-system bond order (P) was assumed to be obtained simply as the sum of the contributions from π' and π'' $(P = P' + P'')$.

The corresponding CC bond distances (r in Å units) were calculated according to the formula[11]

$r = 1.557 - 0.220P/[P + 0.750(1 - P)]$

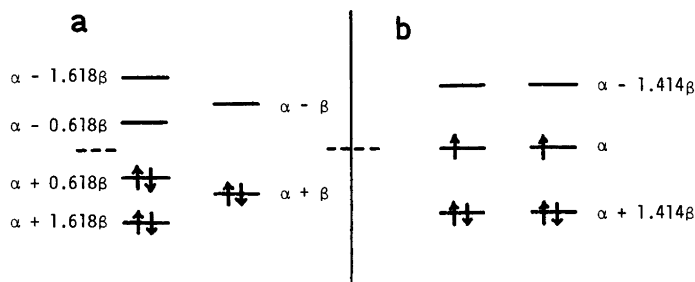The parameters were adjusted to fit the experimental bond lengths of benzene $(P = 0.667)$, ethylene $(P = 1)$

a   b

Fig. 2. The π-system energy levels and π-ground state electron configurations of (a) planar and (b) twisted butatriene.

Table 1. Calculated and observed bond lengths (Å) in butatriene.

Bond	Calculated		Observed	
	Planar	Twisted	Ref. 2	Ref. 4
C=C terminal	1.355	1.389	1.318	—
C=C middle	1.271	1.275	1.283	1.284 ± 0.006

and acetylene $(P=2)$, and the formula has been successfully applied to different hydrocarbons with conjugated and cumulated C=C bonds as well as C≡C bonds.[11] The results of the present case are shown in Table 1 along with the experimental CC bond lengths.[2,4] For the central C=C bond, the calculated bond distances are not much different (0.004 Å) in the two conformations. They agree well with the observed values, the differences being about 0.01 Å. For the terminal C=C bond a marked difference (about 0.03 Å) is found. The value for the planar conformation agrees clearly better with the observed value.

HYPOTHETICAL BUTATRIENE DIRADICAL

The planar structure of monomeric butatriene, as it appears in the gas phase, should not be doubted. The two-dimensional HMO analysis gives additional support to this conclusion. At the same time, however, it suggests that a twisted conformation might be possible. The π-ground state electron configuration (see Fig. 2) shows that twisted butatriene should be a diradical. In this state, the molecule is expected to be highly reactive and readily polymerize. Experimentally, it is found that butatriene is stable at low temperatures but begins to polymerize at about $-30\,°C$.[3] The fact that hydroquinone acts as an inhibitor toward polymerization[1,3] suggests that this is a radical process and triplet butatriene could be the initiator. At temperatures around $0\,°C$, polymerization becomes so rapid that explosive behaviour is encountered.[3] The latter again is consistent with a higher population of the triplet state under these conditions.

With regard to reactivity, it is of interest to compare the chemical properties of butatriene with those of a related compound, cyclobutadiene. Hückel calculations[12] predict that the square configuration of cyclobutadiene should be a triplet. However, it is a generally accepted conclusion that the ground state is a rectangular singlet with

alternating single and double bonds.[13] The reactivity of cyclobutadiene differs significantly from that of butatriene and it has only been observed at very low temperatures.[13] Yet, it is considerably less reactive than butatriene in the gas phase; the half-life has been estimated to be 2 ms at 100 μm,[14] and 10 ms at 35 μm,[15] while butatriene explodes under vacuum.[3] Thus, there seems to be reason to believe that the polymerization of butatriene is much more temperature dependent than the corresponding reaction of cyclobutadiene, *i.e.* dimerization. In either case, it seems clear that the triplet states should be more reactive than the corresponding singlets. Comparison of the activation necessary for the conversions, singlet→triplet, is revealing. The data in Table 1 indicate that only small changes in bond lengths are required for the conversion of planar singlet to twisted triplet for butatriene. The activation process is then simply the rotations around the C_1-C_2 or C_3-C_4 bonds. In the case of cyclobutadiene, the singlet rectangle must undergo considerable changes in bond lengths to reach the square triplet state. This could conceivably explain the differences in reactivity of the two compounds.

It should be possible to prepare transition metal complexes[16] of butatriene. The stabilization of other compounds for which diradical structures are possible, *viz.* cyclobutadiene, trimethylenemethane, and others[17] by complexation with transition metals is well known, but the effect has not so far been studied for butatriene.

Radicals are also known to form ions easily. In the case of butatriene we are predicting the existence of the $C_4H_4^{2+}$ and $C_4H_4^{2-}$ ions, produced by subtracting and adding electrons to the radical in the usual way. It is interesting that the present two-dimensional HMO analysis leads to energetically more stable ions in the twisted conformation than the planar one (*cf.* Fig. 2). The same energy difference is obtained for the positive and negative ions; specifically:

$$E_\pi(\text{ion twisted}) - E_\pi(\text{ion planar}) = 0.421\beta < 0$$

FINAL REMARKS

The purpose of the present work is to demonstrate an application of the extremely simple two-dimensional HMO theory rather than an accurate treatment of butatriene. More sophisticated treatments according to a modified HMO theory[18] or *ab initio* self-consistent field MO calculations[19] are outside the scope of this work. It may be concluded, however, that even this very simple treatment seems to give physically significant results.

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