

THE ELECTRONIC GROUND STATES OF *ORTHO*, *META* AND *PARA*-BENZYNES

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Using CNDO-2 method it was found that the ground state of *ortho* and *meta*-benzyne is singlet, whereas that of *para*-benzyne is a triplet.

In recent years there was accumulated a large body of experimental and some theoretical facts regarding the intermediacy of dehydrobenzenes or arynes.¹ In order to understand and predict various aspects of the physical and chemical behavior of these intermediates it is important to possess the most basic information—the spin state of the most stable form of these molecules. An important approximate SCF method, developed by Pople and coworkers,² appears most suitable to a treatment of the σ and π framework of a molecule such as benzyne. Formally excited states, which will also interest us may be adequately constructed by using virtual orbitals.³

We present in this note some results obtained by the CNDO-2 method² on *ortho*, *meta* and *para*-benzyne. The geometries of these molecules were chosen as initially hexagonal, C—C 1.40 Å, C—H 1.10 Å. The parameters we used were those suggested by Pople and coworkers,² and are summarized in table 1.

The excited states were constructed with configuration interaction between all excitations in a 10 eV range.***) *With this parametrization it turns out that the ground state of ortho and meta-benzyne is a singlet, whereas that of para-benzyne is a triplet.*⁴

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**) Doubly excited configurations were not included in the calculations. They should lower the energy of the lowest singlet states of these molecules.

¹ For a comprehensive review of the chemistry of benzynes see: R. W. HOFFMANN "Dehydrobenzene and Cycloalkynes", Academic Press, New York, 1967.

² J. A. POPLÉ, D. P. SANTRY and G. A. SEGAL, *J. Chem. Phys.*, **43**, S129 (1965); J. A. POPLÉ and G. A. SEGAL, *J. Chem. Phys.*, **43**, S136 (1965); **47**, 3289 (1966).

³ H. W. KROTO and D. P. SANTRY, *J. Chem. Phys.*, **47**, 792 (1967).

⁴ T. YONEZAWA, H. KONISHI and H. KATO, *Bull. Chem. Soc. Japan*, **41**, 1031 (1968) obtained a singlet ground state for *ortho*-benzyne with the triplet 3.73 eV above.

The position of the three lowest singlets and the first triplet are shown in table 2.

Note that whereas *ortho*-benzyne is a clear singlet, the singlet and triplet states of *meta*-benzyne are not far apart in energy. In the series

Table 1
Ionization potentials for S and P orbitals, the resonance integrals (in eV)
and the Slater exponent

Atom	S	P	β_0	Slater exponent
C	-14.05	-5.572	-21.00	1.625
H	-7.176	-	-9.00	1.300

ortho, *meta* and *para* benzyne one can predict a red shift in the lowest singlet-singlet transition.

Assuming that thermodynamic stability will be proportional to the calculated total energy, these calculations place *ortho*-benzyne 1.55 eV below *meta*-benzyne, which in turn is 1.78 eV more stable than the lowest, triplet state of *para*-benzyne.

Table 2
Singlet and triplet energy transitions (in eV)

	Singlet			Triplet
<i>ortho</i> -Benzyne	4.700	5.492	6.497	2.046
<i>meta</i> -Benzyne	4.296	4.435	5.024	0.263
<i>para</i> -Benzyne	3.118	4.722	4.742	-0.760

It appears plausible for these intermediates to discuss their reactivity in terms of frontier controlled reactions.⁵ Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for all of these species are concentrated primarily at the two dehydro carbons. HOMO is lowest for *ortho*-benzyne, and at increasingly higher energy for *meta* and *para* isomers. LUMO exhibits the reverse trend. The actual energy levels are shown in table 3. The trend is in accord with the stability order.

While CNDO-2 calculations do not yield good bond distances, they can predict the direction of distortion from some initially assumed geometry. The overlap populations⁶ which we obtain in calculations assum-

⁵ G. KLOPMAN, *J. Amer. Chem. Soc.*, **90**, 223 (1968).

⁶ R. S. MULLIKEN, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

ing equal C—C bond lengths should be a good indicator of the actual bond length changes which ensue. The results are illustrated below (Fig. 1).

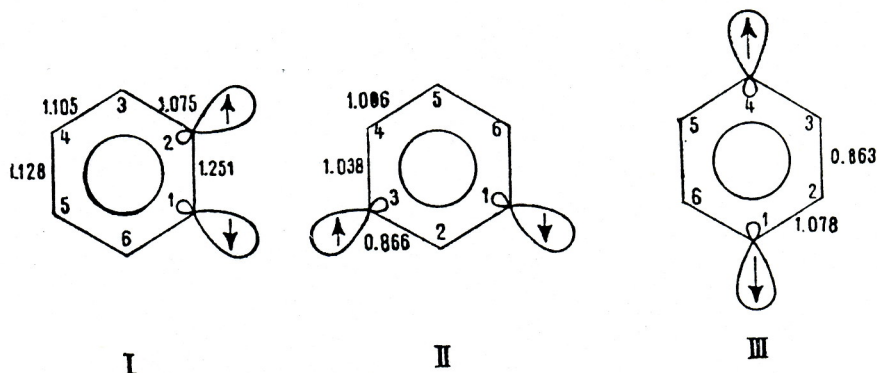


Fig. 1. — Reduced overlap populations for *o*- (I), *m*- (II) *p*-benzyne (III).

The *ortho*-benzyne bond, as expected is the strongest one, followed by the bond opposite and parallel to the partial triple bond. The C₁—C₂ and C₂—C₃ bonds, flanked by the aryne carbons, are expected to be very long in the *meta*-benzyne. In the *para*-benzyne one sees the indications of

Table 3

HOMO and LUMO orbital energy (in eV)

	HOMO	LUMO
<i>ortho</i> -Benzyne	-11.322	0.764
<i>meta</i> -Benzyne	-10.179	-0.598
<i>para</i> -Benzyne	-9.552	-1.398

two allylic fragments, C₆—C₁—C₂ and C₃—C₄—C₅, separated by relatively long bonds. These conclusions parallel the results derived from extended Hückel calculations,⁷ except for the destabilization of *para*-benzyne.

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⁷ R. HOFFMANN, A. IMAMURA and W. J. HEHRE, *J. Amer. Chem. Soc.*, **90**, 1499 (1968)