# The Geometry of the Phenyl Ring in Substituted Benzene Molecules. A Molecular Orbital Approach

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**Abstract:** The distortions of the benzene ring originated by the substituents F, $NO_2$, CN, CCH, and $NH_2$ have been investigated by means of MO SCF semiempirical calculations of PPP and CNDO type. Some bond orders have been analyzed and in particular the MO localized according to the Edmiston and Ruedenberg criterion. The results show two kinds of effects on the ring, both caused by the substituents. A $\pi$ perturbation, which seems to be unimportant except in the $NH_2$ case, manifests itself as a shortening of the 2–3 bond lengths. On the other hand, a rehybridization of the substituted carbon atom decreasing along the series F, $NO_2$, $NH_2$, CN, and CCH shows up as a local $\sigma$ perturbation which implies a shortening of the 1–2 bond lengths along with an opening of the 612 angles. This effect shows a probable dependence upon the group electronegativity. Both effects together account for a semiquantitative agreement with the experimental results. The CNDO bond orders tried seem to become insensitive to the bond-length changes analyzed.

## I. Introduction

The fluorobenzene, nitrobenzene, benzonitrile, phenylacetylene, and aniline $r_s$ structures, calculated from the refined constants in some cases, have been investigated by microwave spectroscopy[1-5] over the last 10 years. In this way, small structural changes caused by the substituents in the phenyl ring from its regular conformation in benzene have been found. These distortions predominantly affect the region near the substituted carbon atom. The most significantly affected geometrical parameters are included in Table 1, as well as those of the benzene molecule[6] to compare them with. The F, $NO_2$, CN, and CCH substituent groups shorten the 1–2 bond lengths and widen the 612 bond angles. The $NH_2$ group on the contrary, gives rise to a shortening of the 2–3 bond length along with a small sharpening of the 612 bond angle. The abovementioned structural changes, which are appreciable in the F and $NO_2$ cases, diminish in the case of benzonitrile and become almost negligible for phenylacetylene and aniline. Nevertheless, in spite of the extremely high precision of the technique utilized, the limitation imposed by the mechanical model bearing the analysis of the experimental data must be kept in mind.

In view of the above experimental structural features, a significant contribution of the resonant ionic forms to the conjugate system description has been suggested as an explanation coherent with the behavior of aniline.[5] The resonance effect, however, was estimated to be unimportant and a local perturbation through the $\sigma$ molecular frame was instead assumed in the other cases studied. A rehybridization process of the substituted carbon atom due to the electronegativity of the substituents has been invoked by Nygaard,[1] Casado,[3] and Cox[4] for this $\sigma$ effect. The rehybridization idea was originally proposed by Bent[7] to account for the structural changes originated by electronegative fluorine. Later, Pappas[8] attempted to verify Bent's conjecture on the basis of a quantitative model, which seems to justify the shortening of the C–C bond length in 1,1-difluoroethylene. A semiquantitative interpretation of the main geometrical changes of the phenyl ring, carried out in the framework of semiempirical SCF MO calculations, is the aim of this paper.

## II. Methodological Aspects

As a preliminary step, $\pi$ bond order calculations were carried out with the PPP method parametrized as proposed by Fischer-Hjalmars et al.,[9-13] to detect the influence of the substituents on the ring conjugate system and hence on the bond lengths. In the same way, CNDO/S AVE calculations were also performed and their results first analyzed in terms of diverse bond orders as defined by Wiberg,[14] Boyd,[15] Ehrenson and Seltzer,[16] and Polansky and Fratev,[17] These bond orders were initially assumed as possible indices of the $\sigma$, $\pi$ and overall effects of the substituents on the bond lengths.

The second and most important step was the transformation of the CNDO/S canonical basis sets into intrinsically localized ones, following the Edmiston and Ruedenberg procedure,[18] These LMO bases were subsequently analyzed in terms of a hybridization model, as a means to the interpretation of the distortions produced in the ring, in accordance with the conjectures of the authors of the experimental work.

A $\sigma$ LMO, $\phi^L{}_{i-j}$, can be approximately represented as

$$\phi^L{}_{i-j} = c_i\psi_{i\to j} + c_j\psi_{i\leftarrow j} \quad (1)$$

where $\psi_{i\to j}$ and $\psi_{i\leftarrow j}$ are hybrid bases on the $i$ and $j$ atoms (Figure 1a). In this way, expanding $\psi_{i\to j}$ in terms of unhybridized basis functions $S$ and $P$ on center $i$

$$\psi_{i\to j} = (1 + \lambda_{i\to j}{}^2)^{-1/2}(S_i + \lambda_{i\to j}P_i) \quad (2)$$

$P_i$ having the required direction, the p character of the $i$ atom in the $i$-$j$ bond should be calculated, as usual, by

$$f_{i\to j} = \lambda_{i\to j}{}^2/(1 + \lambda_{i\to j}{}^2) \quad (3)$$

In the same way, the angle between two hybrid orbitals $\psi_{i\to j}$ and $\psi_{i\to k}$ (Figure 1b) is obtained from the orthogonality condition

$$\lambda_{i\to j}\lambda_{i\to k}\cos\theta_{jik} + 1 = 0 \quad (4)$$

If the loss in the localization process proves to be almost uniformly distributed, it seeems that the normalization to two of the p characters on the same atom does not turn out to be an unrealistic approximation, which allows a better presentation of the results while leaving their meaning unchanged to all intents and purposes of this paper.

## III. Results and Discussion

The numbering sequence always starts from the substituted carbon atom. The calculations were carried out in a Univac 1108 computer by means of programs written in FORTRAN V by the authors of this paper.

**1. Bond Orders.** If the usual bond order–bond length relationship is assumed, the bond-order variations could be taken as the indices of the distortions originated by the substituents

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**Table I.** Experimental Geometrical Data[a]

| X | $d_{1\text{-}2}$ | $d_{2\text{-}3}$ | $d_{3\text{-}4}$ | $\theta_{612}$ | $\theta_{123}$ | ref |
|---|---|---|---|---|---|---|
| H | 0.1397 | 0.1397 | 0.1397 | 120.0 | 120.0 | 6 |
| F | 0.1383 | 0.1395 | 0.1397 | 123.4 | 117.9 | 1 |
| $NO_2$ | 0.1375 | 0.1403 | 0.1396 | 125.0 | 117.1 | 2 |
| CN | 0.138 76 | 0.139 56 | 0.139 74 | 121.82 | 119.00 | 3 |
| CCH | 0.1388 | 0.1396 | 0.1398 | 120.8 | 119.8 | 4 |
| $NH_2$ | 0.1397 | 0.1394 | 0.1396 | 119.4 | 120.1 | 5 |

[a] $d$ in nanometers; $\theta$ in degrees.

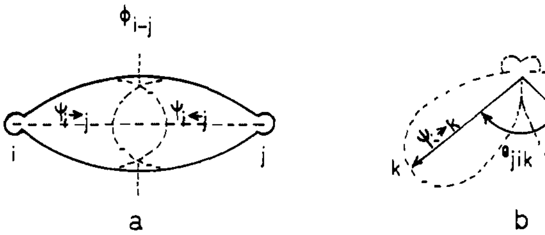

**Figure 1.** LMO and hybridization.

on the bond lengths. A summary of the bond orders is available as supplementary material in Tables S1 and S2.

PPP $\pi$ bond orders account for a shortening of the 2–3 bond lenghts with regard to the 1–2 ones. Other simple and SCF $\pi$ methods utilized have given rise to similar results, which, in addition, do not undergo any sequence changes by arbitrary variations of the substituent parameters. The CNDO/S $\pi$ bond orders also lead to the above bond-lengths relation. Since this behavior is only manifested experimentally by the aniline molecule, it can be assumed that a prevailing $\sigma$ perturbation, originated by the substituents, must be taken into account in the remaining molecules.

Nevertheless, the $\sigma$ CNDO/S bond orders do not account for this $\sigma$ perturbation. In fact, their values for the 2–3 bonds become greater than those for 1–2 ones, with the exception of the Boyd values for the nitrobenzene molecule. The Ehrenson and Seltzer[16] and Polansky and Fratev[17] bond orders, as calculated for fluorobenzene, show the same type of behavior. In this connection, it must be pointed out that a simple addition of the population submatrix elements, $P_{\mu\nu}$, based on the AOs $\mu \in i$ and $\nu \in j$, does not satisfactorily define an $i$-$j$ bond order, on account of its rotational invariance condition. Thus, it is easily shown that the Wiberg bond orders can include antibonding terms as positive contributions and that in the Boyd bond orders, on the contrary, off-diagonal bonding terms are missing. In this situation it may be assumed that the CNDO bond orders tried become insensitive to the $\sigma$ perturbation postulated, probably owing to their own intrinsic limitations. Therefore, the $\sigma$ distortion has to be analyzed from another point of view.

**2. Localized Molecular Orbitals.** As a way of deriving additional understanding about this problem, a LMO analysis in terms of hybridization model, as stated in section 2, has been carried out, assuming for the phenyl ring the standard geometry of the benzene molecule. The $\sigma$ LMOs in the region of the substitution are available as supplementary material in Table S3, along with an index of the localization quality.[19]

The results in Table II show that the $\psi_{2\to1}$ hybrid remains almost unchanged with respect to that of benzene, on account of the local character of the $\sigma$ perturbation. On the contrary, it must be pointed out that the hybrids $\psi_{1\to X}$, $\psi_{1\to2}$, and $\psi_{1\to6}$ show a rehybridization process on the substituted carbon atom, in which the p characters toward the substituent go up, whereas those toward the ring go down, increasing the hybridization $\theta_{612}$ angles (Figure 2). This angle exceeds the theoretical 120° by 2.2° in the benzene molecule, probably due to the bending of the bonds. The degree of the rehybridization proves significant in the fluorobenzene and nitrobenzene cases, whereas it diminishes in the case of benzonitrile and becomes unimportant for phenylacetylene, in agreement with experiment.[20] The $NH_2$ group also accounts for a rehybridization effect of the same type. This $\sigma$ perturbation keeps a good correlation with the $\sigma$ net charges of the substituents (the correlation coefficients for $\theta_{612}$-$Q_\sigma$ and $f_{1\to2}$-$Q_\sigma$ are 0.99 and 0.98, respectively), showing a probable dependence upon the group's electronegativity.

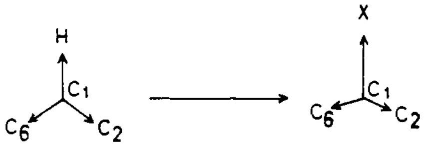

**Figure 2.** Rehybridization originated on $C_1$ by the substitution ($f_{1\to}$, $\theta_{612}$).

CNDO/S calculations were repeated for the above five derivatives, this time on the basis of their microwave experiment geometries. The results for the $\sigma$ perturbation in the region of the substitution are also summarized in Table II. However, the semiquantitative features of the results obtained were those shown for the standard geometries in all cases. CNDO/2 parametrization was also utilized. In this way 124.7 and 124.6° were obtained for the $\theta_{612}$ angle in the aniline case, from a planar standard geometry and from the experimental one, respectively.

The closeness between the results obtained from standard geometries and those obtained from experimental ones must be emphasized. With regard to this, it must be pointed out that, as the changes in total energy accompanying the changes from standard to experimental geometries (Table II) are not extremely high and keep the right direction, so the standard geometries may be an acceptable substitute for experimental geometries, particularly in dealing with molecular properties which do not show high sensitivity to geometrical changes, like some of those related to the population matrix elements.

The analysis of the LMOs from a hybridization point of view clearly shows a local $\sigma$ perturbation originated by the substituents on the next ring carbon atom. If the usual p character–bond length relationship is assumed,[21] this perturbation could account for the experimental results in a semiquantitative way, in spite of uncertain bond bending contributions, supposing that it overcomes the $\pi$ contribution, except in the aniline case.

The canonical $\pi$ orbitals were localized along with the $\sigma$ ones. A list of the localized $\pi$ orbitals is available as supplementary material in Table S4. The results show a set of three orbitals of type $\pi$l3 for the ring (essentially a three-center LMO with a smaller contribution from the C atom farthest away). These orbitals are $\pi l3C_6C_1C_2$, $\pi l3C_2C_3C_4$, and $\pi l3C_4C_5C_6$ for the benzene, fluorobenzene, nitrobenzene, and benzonitrile molecules and $\pi l3C_1C_2C_3$, $\pi l3C_3C_4C_5$, and $\pi l3C_5C_6C_1$ for the phenylacetylene and aniline molecules. In addition, there is another set for the $\pi$ pairs of the substituent groups. Some general remarks can be inferred from a brief analysis of the above localized $\pi$ orbitals. The LMOs describing the $\pi$ pairs of the substituents are delocalized to a very small degree toward the ring. The $NH_2$ group stands out in virtue of its delocalization being two or three times higher than

**Table II.** $\sigma$ LMO and Hybridization in the $C_1$ Atom[a]

| X | $f_{2\rightarrow 1}$ A | $f_{1\rightarrow 2}$ A | $f_{1\rightarrow 2}$ B | $f_{1\rightarrow X}$ A | $f_{1\rightarrow X}$ B | $n(sp^n)$ A | $n(sp^n)$ B | $\theta_{612}$ A | $\theta_{612}$ B | $Q_\sigma(X)$ A | $Q_\sigma(X)$ B | $\Delta E^b$ A → B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 0.652 | 0.652 | | 0.696 | | 1.87 | | 122.2 | | | | |
| F | 0.656 | 0.607 | 0.600 | 0.787 | 0.801 | 1.54 | 1.50 | 130.5 | 131.9 | −0.235 | −0.233 | −1.18 |
| $NO_2$ | 0.654 | 0.629 | 0.615 | 0.742 | 0.771 | 1.70 | 1.60 | 126.2 | 128.8 | −0.152 | −0.154 | −1.36 |
| CN | 0.655 | 0.649 | 0.644 | 0.703 | 0.713 | 1.85 | 1.81 | 122.8 | 123.6 | −0.113 | −0.117 | −0.95 |
| CCH | 0.654 | 0.652 | 0.650 | 0.696 | 0.700 | 1.87 | 1.86 | 122.3 | 122.5 | −0.084 | −0.085 | −0.04 |
| $NH_2$ | 0.654 | 0.639 | 0.642 | 0.722 | 0.716 | 1.77 | 1.79 | 124.4 | 123.9 | −0.116 | −0.101 | −0.02 |

[a] $\theta$ in degrees; $\Delta E$ in electron volts. A = standard geometries; B = experimental geometries. [b] Core repulsion energy calculated as $\Sigma_i \Sigma_{j>i} \{\lambda_{ij}(Z_iZ_j/r_{ij}) + (1 - \lambda_{ij})Z_iZ_j\gamma_{ij}\}$, $Z_i$ and $Z_j$ being the $i$ and $j$ core charges and $\gamma_{ij}$ the two-center electron repulsion integral. $\lambda_{ij} = \exp(-\alpha_{ij}r_{ij})$, where $\alpha_{ij}$ is a parameter for the $ij$ pair.

**Table III.** Heteroatom Quantum Parameters and Distortion Effects[a]

| X | $U_{s(X)}$ | $U_{p(X)}$ | $\beta_{(X)}$ | $\theta_{612}$ | $P^{(W)}{}_{1-2}$ | $P^{(W)}{}_{2-3}$ | $P^{(B)}{}_{1-2}$ | $P^{(B)}{}_{2-3}$ | $Q_\sigma(X)$ | $Q_\pi(X)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | −199.3 | −178.1 | −39.0 | 130.5 | 1.428 | 1.447 | 1.759 | 1.773 | −0.235 | 0.018 |
| F | −211.0 | −189.0 | −39.0 | 136.9 | 1.443 | 1.437 | 1.772 | 1.768 | −0.525 | 0.009 |
| | −199.3 | −178.1 | −60.0[b] | 127.9 | 1.412 | 1.453 | 1.750 | 1.777 | −0.190 | 0.029 |
| | −199.3 | −178.1 | −27.0 | 134.3 | 1.441 | 1.437 | 1.778 | 1.767 | −0.277 | 0.012 |
| | −73.36 | −61.32 | −26.0 | 126.2 | 1.411 | 1.451 | 1.759 | 1.776 | −0.152 | −0.029 |
| N | −80.00 | −68.00 | −26.0 | 129.6 | 1.418 | 1.448 | 1.763 | 1.774 | −0.336 | −0.026 |
| $(NO_2)$ | −73.36 | −61.32 | −18.0 | 129.2 | 1.424 | 1.443 | 1.777 | 1.770 | −0.233 | −0.017 |

[a] $U$, $\beta$ in electron volts; $\theta$ in degrees. W = Wiberg; B = Boyd. [b] Value utilized by Yadav et al.[25]

those of the other groups. The $\pi$ net charges of the substituents indicate their donor or acceptor nature and constitute an index of the $\pi$ perturbation they originate. Although these charges are very small, that of the $NH_2$ group must again be emphasized, being three or four times higher than those of the remaining ones, in accord with the conclusions of Bernardi et al.[22] On the other hand, the delocalization of the ring $\pi$ orbitals toward the substituents is nearly null in fluorobenzene and aniline and presents small values in the other derivatives.

The above remarks seem to confirm that the $\pi$ perturbation does not become relevant except in the aniline molecule, for which the results are consistent with a significant role of the resonant ionic forms. The weight of these forms seems to be smaller in the nitrobenzene and benzonitrile molecules and of no account for fluorobenzene. As the substituents have a common parent substrate, the phenyl ring, their dependence upon it, stated by Bernardi et al.,[23] becomes standardized.

**3. Some Factors Affecting the Degree of the Distortion.** Even if semiempirical methods should be taken as "phenomenological simulation procedures," as stated by Malrieu,[24] we have nevertheless carried out several calculations which may serve to indicate those substituent group heteroatom factors which affect the distortion of the phenyl ring. The main results are listed in Table III. It is shown that the above structural changes become more pronounced as the absolute values of the monocentric penetration integrals, $U_X$, increase and also as those of the atomic parameter, $\beta_X$ related to the resonance integral, $\beta_{1-X}$, decrease. In both cases the calculations carried out give the same picture for the changes in the substituted region of the ring: the p character $f_{1\rightarrow 2}$ falls, whereas the bond angle $\theta_{612}$ increases. On the other hand, a significant increment of the electronic charge on the heteroatoms as well as a greater localization of its $\pi$ pairs takes place when $U_X$ is incremented, indicating a dependence on the X electronegativity. The influence of the $\beta_X$ parameter seems, on the contrary, to bear no relation to any classical effect. Finally, it must be pointed out that Wiberg and Boyd bond orders approach the experimental bond length sequence as the heteroatom $\sigma$ effect increases. It seems therefore that the above bond orders should be taken as insensitive to the minimal changes undergone by the bond lengths, due to their intrinsic limitations.

## IV. Concluding Remarks

The calculations carried out clearly show two kinds of competitive effects originated by the substituents: (1) a $\pi$ effect which increases the bond length $d_{1-2}/d_{2-3}$ ratio in the ring (this effect seems to decrease as the substituent group electronegativity increases and it is of importance mainly in the aniline molecule); (2) a local $\sigma$ effect, which may be understood in terms of a hybridization model on the substituted carbon atom and which implies a shortening of the $d_{1-2}$ bond lengths along with an opening of the $\theta_{612}$ bond angles, through a diminution of the p character toward the ring. This effect, on the contrary, seems to increase with the substituent group electronegativity and it keeps a semiquantitative correlation with the experimental changes, except in the case of aniline. Both effects together add up to a semiquantitative interpretation of the experimental results agreeing with the suggestions[1-5] mentioned at the beginning of this paper.

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**Supplementary Material Available:** Bond orders (Tables S1 and S2), $\sigma$ LMO (Table S3), and $\pi$ LMO (Table S4) (3 pages). Ordering information is given on any current masthead page.

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(19) The index $I_{I-J}$ for a $\phi^{L}{}_{I-J}$ LMO can be set up through the deviation of the $\phi^{L}{}_{I-J}$ from a completely localized one, $\phi^{CL}{}_{I-J}$, as is shown in the equation $I_{I-J} = \frac{1}{2}\langle(\phi^{L}{}_{I-J} - \phi^{CL}{}_{I-J})^2\rangle$.
(20) The calculated sequence, F > $NO_2$, which is inverted with respect to the experimental results, could, in fact, be due to Pople's value of 39 eV having been used for the $\beta_F$ parameter instead of del Bene and Jaffé's. As will be shown later, the rehybridization effect diminishes as the absolute value of this parameter increases. However, within a semiquantitative discussion of the structural changes, this feature of the results does not seem relevant.
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# Theoretical Studies of the Structures and Reactions of Substituted Carbonyl Ylides

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**Abstract:** The electronic structures and geometries of model substituted carbonyl ylides containing amino, cyano, and phenyl substituents were investigated by ab initio SCF calculations using the STO-3G and 4-31G basis sets and 3 × 3 CI. Stabilization and geometrical distortions caused by substituents, barriers to isomerization, the ease of formation of carbonyl ylides from oxiranes, the regioselectivity of fragmentations of carbonyl ylides, and the regioselectivities and reactivities of cycloadditions of substituted carbonyl ylides were investigated.

## Introduction

In 1965, Linn and Benson discovered that tetracyanoethylene oxide undergoes cycloadditions to alkenes across the CC single bond. Kinetic studies implicated the formation of a reactive intermediate, now known definitely to be a carbonyl ylide.[2] Earlier, Ullman and Milks observed the formation of relatively stable cyclic carbonyl ylides upon thermolysis, or photolysis, of an indenone oxide.[3] In 1967, Griffin and coworkers discovered the photochemical fragmentation of oxiranes,[4] and later showed that carbonyl ylides were detectable intermediates upon photolysis of oxiranes in low-temperature glass matrices.[5,6] Huisgen and co-workers studied the thermal cycloadditions of oxiranes, and proved beyond doubt that carbonyl ylides are intermediates in these reactions.[7] The chemistry of substituted carbonyl ylides is summarized in Figure 1.

Several theoretical studies of the parent carbonyl ylide (2-oxatrimethylene) and its formation from oxirane have been reported, and during the course of our work Bigot, Sevin, and Devaquet reported high-level ab initio calculations on the parent oxirane–carbonyl ylide interconversion and the fragmentation of oxirane and carbonyl ylide to carbonyl and carbene fragments.[8,9] Our investigation forms a natural complement to the reports by these authors, since we have concentrated on the influence of substituents on energies of the various species and processes shown in Figure 1.

In this paper, we attempt to establish a number of details about carbonyl ylides which only can be indirectly inferred from experiment. In particular, using ab initio SCF calculations[10] with the STO-3G[11] and 4-31G[12] basis sets, and 3 × 3 CI,[13] we have attempted to answer the following questions: (1) How do substituents facilitate the thermal ring opening? (2) How do substituents influence the geometries and the barriers to isomerization of carbonyl ylides? (3) How do substituents influence the reactivities and regioselectivities of carbonyl ylides in cycloaddition reactions? (4) Are fragmentations of substituted carbonyl ylides thermal or photochemical processes? (5) What controls the direction of the fragmentation?

**Molecular Orbitals of Carbonyl Ylide.** The high-lying filled and low-lying vacant molecular orbitals of the parent carbonyl ylide primarily located on heavy atoms are shown in Figure 2. In addition to the familiar allyl-anion-like $\pi$ molecular orbitals, $\pi_1$, $\pi_2$, and $\pi_3{*}$, the valence orbitals of the heavy-atom skeleton of the planar molecule include filled oxygen lone-pair and CO bonding orbitals, as well as vacant CO antibonding orbitals. The last two appear as combinations which are symmetry adapted with respect to the symmetry plane bisecting the molecule. In our discussion, we will describe the planar geometry as the 0°,0° conformation, following Hoffmann's nomenclature.

Upon a 90° rotation of one $CH_2$ to form the 0°,90° conformation, $\pi_1$, $\pi_2$, and $\pi_3{*}$ correlate with the $\pi_{CO}$, the carbon lone pair ($n_C$), and $\pi{*}_{CO}$ orbitals, respectively, while double rotation to the 90°,90° geometry gives two carbon lone pairs and the out-of-plane oxygen long pair. However, since the highest occupied molecular orbital (HOMO) and the lowest unoccupied MO (LUMO) are close in energy, the molecule may have appreciable diradical character. That is, it may prove necessary to describe this molecule as a linear combination of the ground configuration shown ($\ldots\pi_2{}^2\pi_3{*}^0$) and a doubly excited configuration ($\ldots\pi_2{}^0\pi_3{*}^2$).

Whereas a closed-shell description of a diradical species overestimates the zwitterionic character of the wave function, a linear combination of the ground and double excited configurations eliminates much of this zwitterionic character.[14] Hayes and Siu carried out 2 × 2 configuration interaction calculations on the parent carbonyl ylide and found that the ground state was composed of 81% of the ground configuration and 19% of the doubly excited configuration.[15] They described carbonyl ylide as a molecule with 38% (=2 × 19%) diradical

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