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Conformational instability of the lowest triplet state of the benzene nucleus.

II. p-Xylene, the influence of substituents

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A calculation of the potential-energy surface of the lowest triplet state of p-xylene as a function of the $S_8(\rho, \varphi)$ distortion coordinate of the benzene skeleton has been made to learn more about the influence of substituents on the vibronically induced distortion of benzene in its metastable triplet state. The results show the hexagonal conformation of the benzene nucleus in p-xylene to be unstable with respect to distortions along $S_8(\rho, \varphi)$. In contrast with benzene, for which a flat, virtually cylindrical trough was calculated, the lowest triplet state of p-xylene shows a preference for quinoidal conformations. The variation in energy with the position of the methyl groups in the quinoidal structure is insignificant within the accuracy of the calculation.

I. INTRODUCTION

In the past EPR and electron-nuclear double resonance experiments have shown that in a solid the lowest triplet state of benzene does not possess hexagonal symmetry.¹⁻³ This lowering of symmetry has been interpreted⁴⁻⁶ as the result of vibronic coupling between the $^3B_{1u}$ and the $^3E_{1u}$ states via the e_{2g} vibration ν_8 , first considered by Moffitt and Liehr.⁷ In the crystalline or glassy samples used in these experiments, however, the molecule is subject to the anisotropy of the environment, which lowers the symmetry and modifies the potential-energy surface of the $^3B_{1u}$ state. Since experimental material that could provide information on the distortion of the free molecule in the lowest triplet state does not exist, it was not clear to what extent the crystal field plays a role in the distortion.

Recently, we reported calculations on the vibronic coupling in the $^3B_{1u}$ and $^1B_{1u}$ states of benzene.⁸⁻⁹ These calculations demonstrated that both states are unstable with respect to a S_8 distortion, the symmetry coordinate dominant in ν_8 , and the trough which surrounds the energy maximum belonging to the D_{6h} conformation did not show any significant variations in depth with period $2\pi/3$ which in the past were often thought to be present.

Here we shall be concerned with another kind of perturbation that can affect the distortion of the benzene molecule in its lowest triplet state, the influence of substituents. McWeeny and Peacock have already pointed out that the vibronic coupling between the B_{1u} and E_{1u} states should persist, as long as the substituents do not appreciably disrupt the electronic character of the benzene skeleton.¹⁰ Consequently, there is reason to expect that also in the lowest triplet state of such derivatives the benzene nucleus is unstable with respect to an $S_8(\rho, \varphi)$ distortion.

For many substituted benzenes magnetic resonance experiments have revealed that the nucleus deviates considerably from hexagonal symmetry in the lowest triplet

state.¹¹⁻¹⁹ In particular, experimental efforts have been devoted to the characterization of the lowest triplet state of several methyl substituted benzenes: toluene,¹⁴ p-xylene,¹⁵ and mesitylene.¹² Originally it was thought that, depending on the substitution pattern of the molecule considered, either the quinoidal or antiquinoidal conformation would be stabilized. This assumption seemed to be corroborated by the experiments on mesitylene¹² in which a quinoidal distortion was observed in EPR experiments on the lowest triplet state. Subsequent experiments on toluene¹⁴ and p-xylene¹⁵ revealed distortions that were neither antiquinoidal nor quinoidal. Ultimately it was concluded¹⁶ that the distortions in toluene and p-xylene could be interpreted on the basis of a stabilization by methyl groups of the allyl-like fragments which constitute the antiquinoidal conformation.

Here we report *ab initio* calculations on the lowest triplet state of p-xylene, performed to study the influence of methyl substituents on the distortion of the benzene nucleus on excitation to this state. It will be shown that p-xylene in its lowest triplet state is not stable with respect to $S_8(\rho, \varphi)$ distortions. The trough which surrounds the hexagonal conformation is not φ independent as it is for benzene, where it has a virtually constant depth of some 800 cm^{-1} . The quinoidal conformations in p-xylene are stabilized by 1600 cm^{-1} with respect to the hexagonal conformation and the antiquinoidal conformations by only 200 cm^{-1} . It further appears that previous arguments about the stabilization by the substituents are not able to explain the results of our calculations.

II. COMPUTATIONAL DETAILS

As in our previous calculations on the B_{1u} states of benzene, we will assume that the vibronic coupling in the lowest triplet state of p-xylene occurs via the e_{2g} symmetry mode S_8

(Ref. 20) of the benzene skeleton. This mode can be expressed in polar coordinates as⁷

$$\begin{aligned} Q_{8a} &= \rho \cos \varphi, \\ Q_{8b} &= \rho \sin \varphi; \end{aligned} \quad (1)$$

see Fig. 3 of paper I (Ref. 9) for the change in geometry with ρ and φ . For $\varphi = 0^\circ, 120^\circ$, and 240° the quinoidal conformations are generated, while for $\varphi = 60^\circ, 180^\circ$, and 300° the antiquinoidal conformations are obtained (see Fig. 1). In benzene, for a given ρ , the three quinoidal conformations on symmetry grounds are of the same energy and similarly the three antiquinoidal conformations. In p-xylene this is no longer true. If the quinoidal conformation is considered as a biradical the methyl groups are substituted at the carbon radical atoms for $\varphi = 0^\circ$, or at one of the carbon atoms of the double bond for $\varphi = 120^\circ$ and 240° . When regarding the antiquinoidal conformation as two allyl-like fragments these are substituted either at the central carbon atoms for $\varphi = 180^\circ$, or at the terminal positions for $\varphi = 60^\circ$ and 300° .

In the calculations on p-xylene we used the same geometry of the benzene skeleton as before ($R_{CC} = 1.440 \text{ \AA}$; $R_{CH} = 1.085 \text{ \AA}$).^{8,9} Note that the R_{CC} distance is not the distance found for the ground state of benzene, but a distance optimized to give the lowest energy of the ${}^3B_{1u}$ state of benzene in D_{6h} symmetry. The C-C bonds to the methyl group have been directed along the original CH directions with distances determined in experiments on the ground state.²¹ $R_{C_{ring}-C_{methyl}} = 1.512 \text{ \AA}$; $R_{C_{methyl}-H_{methyl}} = 1.113 \text{ \AA}$. In the context of this article we will define the hexagonal conformation of p-xylene as p-xylene with a hexagonal benzene skeleton.

The larger part of our calculations, referred to as C_{2h} calculations, use an orientation of the methyl groups with respect to the benzene ring in which one of the methyl hydrogen atoms lies in the plane of the ring, with the two methyl groups oriented such that the symmetry remains C_{2h} for all quinoidal and antiquinoidal conformations. In these molecular geometries the axis perpendicular to the plane of the ring is a twofold axis and the plane of the ring is a plane of symmetry. For $\varphi = 0^\circ$ and 180° some calculations have also been performed with different rotational orientations of the substituents.

The atomic-orbital (AO) basis set used was identical to that described before. With this basis set we obtain a self-consistent-field (SCF) energy of -308.6591 H for the ground state of the hexagonal conformation.

The configuration-interaction (CI) calculations used the CRAY-XMP version of the Wuppertal-Bonn multireference, single- and double-excitation configuration-interaction (MRDCI) method with configuration selection and energy extrapolation to the generated MRDCI space.²² An estimate of the energy corresponding to the full CI space within the AO basis was made according to Ref. 23. For the CI the set of 100 molecular orbitals (MOs) was truncated to 58 by discarding the 42 orbitals of higher orbital energy. Furthermore, the lower 18 σ orbitals were kept doubly occupied resulting in a CI in which 22 electrons were correlated.

The degeneracy of the MOs present in the D_{6h} symmetry of benzene is removed in p-xylene. Consequently, its low-

est triplet state, even with a hexagonal benzene nucleus, is no longer a two-configuration state with equal coefficients. For the CI calculations on benzene we have used the SCF orbitals of the ${}^5A_{1g}$ state [$\cdots(1a_{2u})^2(1e_{1g})^2(1e_{2u})^2$] to circumvent the problems associated with such a two-configuration state. For p-xylene we have used the triplet MOs resulting from an SCF calculation on the dominant configuration in the CI expansion.

The lowest triplet state has been studied using a set of the 18 reference configurations that had a coefficient larger than 0.05 in the CI expansion for this state. Selection on the lower two roots of the zeroth-order CI expansion with an energy threshold of $10 \mu\text{H}$ resulted in CI expansions into 3000–8000 configurations out of 1 026 078 generated configurations.

III. RESULTS AND DISCUSSION

In this section we shall first present and discuss the results of the C_{2h} calculations from which we obtain the dependence of the energy and wave functions of the lowest triplet state on φ . Subsequently, calculations will be discussed in which the influence of the orientation of the substituents with respect to the benzene ring is investigated.

In Fig. 1 the potential-energy surface of the lowest triplet state of p-xylene is reproduced for distortions along the $S_8(\rho, \varphi)$ distortion coordinate for four values of φ . In Table I some characteristics of the calculation on the hexagonal conformation are given.

As can be seen from Fig. 1 the basic features of the potential-energy surface of the ${}^3B_{1u}$ state of benzene are preserved: the hexagonal conformation is no longer that of minimum energy, the minimum occurring for distorted conformations with $\rho = 0.020 \text{ \AA}$ (cf. 0.0185 \AA in benzene). In contrast with the potential-energy surface of benzene, for which we calculated an almost cylindrical trough with a depth of 800 cm^{-1} , the bottom of the trough in the potential-

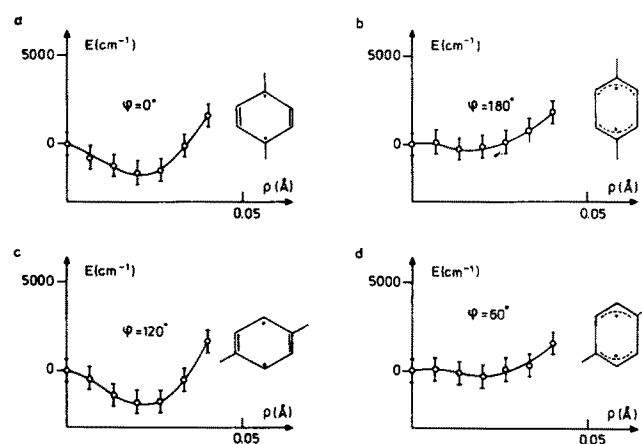


FIG. 1. Potential-energy surface for the lowest triplet state of p-xylene along the $S_8(\rho, \varphi)$ distortion coordinate. The zero of energy is defined as the energy of the lowest triplet state for the hexagonal conformation. (a) $\varphi = 0^\circ$. (b) $\varphi = 180^\circ$. (c) $\varphi = 120^\circ$ (equivalent to $\varphi = 240^\circ$). (d) $\varphi = 60^\circ$ (equivalent to $\varphi = 300^\circ$).

TABLE I. Characteristics of the CI calculation of the lowest triplet state of p-xylene for the hexagonal conformation of the benzene skeleton ($1H = 219\,474.62\text{ cm}^{-1}$).

No. reference configurations	18
No. generated configurations	1 026 087
Threshold T (μH)	10
No. selected configurations at T	5252
E_{rc}^a (H)	-308.5630
$E(T)^b$ (H)	-308.6652
$E(T=0)^c$ (H)	-308.7226
Extrapolation uncertainty (H)	0.0029
$E(T=0) + E_{DAV}^d$ (H)	-308.7348
$\sum_{i=1}^{ref} c_i^2$ ^e	0.9233

^a Energy after CI with only the reference configurations.

^b Energy at the threshold T .

^c Energy extrapolated to $T=0$.

^d Energy extrapolated to $T=0$ including the Davidson correction (Ref. 23).

^e Sum of squared contributions of the reference configurations in the final CI expansion.

energy surface of the lowest triplet state of p-xylene exhibits considerable energy variations. The quinoidal minimum is now 1700 cm^{-1} lower than the hexagonal conformation, while the antiquinoidal minimum is only 200 cm^{-1} lower. The hexagonal conformation is not exactly a local maximum on the potential-energy surface, and the values of ρ for which the minima occur for $\varphi = 0^\circ \pmod{120^\circ}$ and $\varphi = 180^\circ \pmod{120^\circ}$ are not quite equal, probably because the bond length in the ring has been taken equal to that for benzene in the $^3B_{1u}$ state.

Figure 1 does not demonstrate a significant difference in energy between the three antiquinoidal conformations or between the three quinoidal ones. This is somewhat surprising since it has often been thought that a stabilization of the antiquinoidal conformation for $\varphi = 60^\circ$ and 300° would occur and a stabilization of the quinoidal conformation for $\varphi = 0^\circ$.²⁴ The antiquinoidal conformation is commonly looked upon as resembling two allyl-like fragments. For $\varphi = 60^\circ$ and 300° the methyl groups in these fragments occupy a terminal position, which should be favored over the center position occupied for $\varphi = 180^\circ$. The quinoidal conformation, on the other hand, may be compared with a biradical. For $\varphi = 0^\circ$ tertiary radicals are generated which should be more stable than the secondary radicals obtained for $\varphi = 120^\circ$ and 240° . We shall come back to this point later.

The results for the hexagonal conformation already suggest a stabilization of the quinoidal minimum by the methyl groups. In the CI expansion for the lowest triplet state in this geometry the configuration dominant for quinoidal conformations has a much larger coefficient than that for antiquinoidal conformations: $c_Q^2 = 0.64$, $c_A^2 = 0.19$ [the definition of these two configurations is given in Fig. 2(a)]. This effect parallels the trends in the orbital energies. In Fig. 2 we have depicted the energies of the important π orbitals for the ground state of benzene [Fig. 2(a)] and those for the ground state of p-xylene [Fig. 2(b)]. The methyl group is considered to be electron repelling.²⁵ Indeed we observe that the orbital energies of the π MOs are shifted by an amount

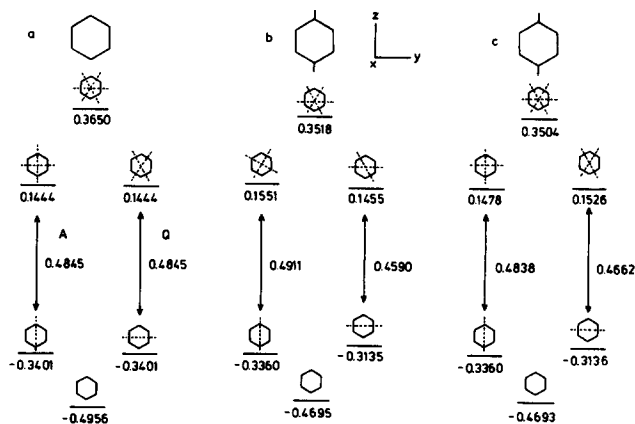


FIG. 2. Comparison of the π orbitals in the ground state of p-xylene with the corresponding orbitals in the ground state of benzene for the hexagonal conformation of the two molecules. Orbital energies are given in atomic units. A and Q denote the configurations dominant in antiquinoidal conformations and quinoidal conformations. (a) Benzene. (b) p-xylene with methyl groups oriented such that the x axis is a twofold axis and the yz plane is a symmetry plane. Note the symmetry breaking of the SCF virtual orbitals. (c) p-xylene with methyl groups oriented such that the y axis is a twofold axis and the xz plane is a symmetry plane.

that depends on the extent to which the AOs on the atom carrying the methyl group participate in the MO concerned. Unlike in the classical Hückel picture, in which the shift for occupied and virtual orbitals would be the same, here the occupied orbitals are shifted more than the virtual orbitals. Because of the unequal shifts the energy difference between the singly occupied MOs of the quinoidal configuration becomes less than the difference between those of the antiquinoidal configuration. Though we are aware that this energy difference is only one of the effects determining the energy of the lowest triplet state, the observation that it is less for the quinoidal excitation than for the antiquinoidal excitation would seem to support the observed preference for quinoidal structures.

Figure 2(b) reveals that the methyl groups, apart from the shifts in the orbital energies, also have a marked influence on the wave functions. Though the D_{6h} symmetry of the benzene skeleton itself is preserved, the substitution generates a reduction in symmetry of the SCF orbitals. The nodal planes in the virtual π orbitals, though still present, are rotated by 60° with respect to the related orbitals in benzene. This results in a situation where the virtual orbital associated with the quinoidal configuration is even lower in energy than that associated with the antiquinoidal one. We note, however, that the energy difference between the two configurations is primarily determined by the energy shifts of the doubly occupied orbitals.

Mulliken population analyses for the lowest triplet state of p-xylene show that, as in benzene, the total population on an atom, i.e., the appropriate sum of diagonal and off-diagonal elements of the density matrix, hardly varies as a function of the distortion. The most important difference with the populations in the lowest triplet state of benzene is that the carbon atoms carrying the methyl groups have significantly less population (-0.15) than those to which a hy-

drogen is attached. This is observed in the ground state as well as in the lowest triplet state. Ermler and Mulliken also noted this change in a study of the ground state of toluene and found it to originate in a transfer of the σ bond population into the methyl group.²⁶

When the total population on an atom is divided into the population on the atom itself and the populations in the bonds, large changes occur in these populations as a function of the distortion. In Fig. 3 we have plotted the population differences between the lowest triplet state of p-xylene and the ground state of benzene for those populations on atoms and in bonds that change most in the distortion process. Here it is important to note that for the ground state of benzene these populations hardly change. In Table II a comparison is made between the population differences in the lowest triplet state of benzene [Table II(a)] and in the lowest triplet state of p-xylene [Table II(b)] for the hexagonal conformation and for two distorted structures with $\rho = 0.020 \text{ \AA}$, $\varphi = 0^\circ$ and $\rho = 0.020 \text{ \AA}$, $\varphi = 180^\circ$. The numbering of the atoms in this table is the same as the numbering in Fig. 3(a). We first consider the populations for the hexagonal conformation. The quinoidal configuration dominates in the CI

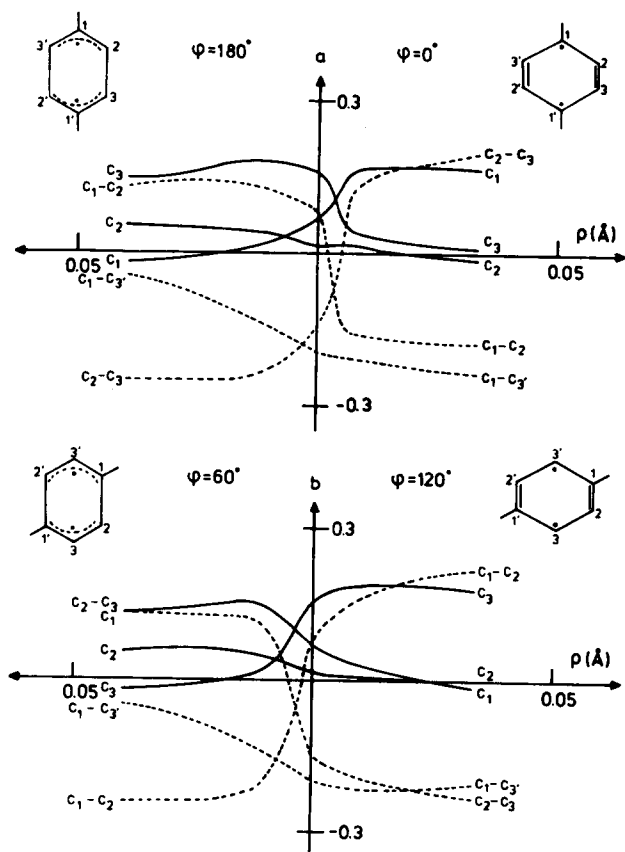


FIG. 3. Dependence of the populations in bonds (C_{i-j}) and on atoms (C_i) on the $S_8(\rho, \varphi)$ distortion. Plotted are the differences between the populations in the lowest triplet state of p-xylene and the corresponding ones in the ground state of benzene. (a) $\varphi = 180^\circ$ and $\varphi = 0^\circ$. (b) $\varphi = 60^\circ$ and $\varphi = 120^\circ$.

TABLE II. Populations on atoms (C_i) and bonds (C_{i-j}) in the lowest triplet state of benzene (a) and p-xylene [(b) and (c)]. Cases (b) and (c) differ in the rotational orientation of the methyl groups with respect to the ring. In this table the absolute populations are not given but the populations relative to the corresponding populations in the ground state of benzene are. The atoms are numbered as in Fig. 3(a). The axes system xyz is defined in Fig. 2.

	(a) Benzene		
	$\rho = 0.02 \text{ \AA}$ $\varphi = 180^\circ$	$\rho = 0.00$	$\rho = 0.02 \text{ \AA}$ $\varphi = 0^\circ$
C_1	+ 0.015	+ 0.105	+ 0.195
C_2	+ 0.140	+ 0.105	+ 0.055
C_3	+ 0.140	+ 0.105	+ 0.055
C_{1-2}	- 0.025	- 0.120	- 0.210
C_{1-3}	- 0.025	- 0.120	- 0.210
C_{2-3}	- 0.280	- 0.120	+ 0.090

	(b) p-xylene C_{2h} (C_2^x, σ_{yz})		
	$\rho = 0.02 \text{ \AA}$ $\varphi = 180^\circ$	$\rho = 0.00$	$\rho = 0.02 \text{ \AA}$ $\varphi = 0^\circ$
C_1	+ 0.005	+ 0.070	+ 0.170
C_2	+ 0.045	+ 0.015	+ 0.000
C_3	+ 0.175	+ 0.160	+ 0.020
C_{1-2}	+ 0.140	+ 0.085	- 0.170
C_{1-3}	- 0.115	- 0.195	- 0.205
C_{2-3}	- 0.250	- 0.145	+ 0.170

	(c) p-xylene C_{2h} (C_2^y, σ_{zx})		
	$\rho = 0.02 \text{ \AA}$ $\varphi = 180^\circ$	$\rho = 0.00$	$\rho = 0.02 \text{ \AA}$ $\varphi = 0^\circ$
C_1	- 0.030	+ 0.140	+ 0.180
C_2	+ 0.125	+ 0.055	+ 0.015
C_3	+ 0.125	+ 0.055	+ 0.015
C_{1-2}	+ 0.025	- 0.155	- 0.195
C_{1-3}	+ 0.025	- 0.155	- 0.195
C_{2-3}	- 0.275	+ 0.055	+ 0.175

expansion for this conformation (see below), which is reflected accordingly in the population distribution. Two of the bonds of the benzene nucleus become stronger than in the unsubstituted molecule, four bonds become weaker, and a localization occurs on two of the carbon atoms [compare Tables II(a) and II(b)].

Next we regard the changes in the populations upon distortion. In Fig. 3 we see for the quinoidal side qualitatively the same behavior as in benzene: a localization occurs such that the π electronic structure of the benzene skeleton resembles a biradical. We note from Table II, however, that the double-bond character is manifested more in p-xylene than it is in benzene. The changes on the antiquinoidal side do not conform to the variation of the populations found in benzene (see also Table II). In the lowest triplet state of benzene we observed that for the antiquinoidal geometries two allyl-like fragments were formed upon distortion. In the lowest triplet state of p-xylene an even further localization occurs within the allyl radical since the population in one of the bonds of the allyl radical becomes considerably higher than in the other bond, in accordance with the reduction in

orbital symmetry noted in Fig. 2(b). By this effect the final distribution approaches that of the quinoidal form and the only resemblance to the antiquinoidal form of benzene is the weakening of the long bond.

As we saw the calculations revealed an unexpected indifference of the energy to the position of the methyl groups in the quinoidal and antiquinoidal conformations. In order to verify that this is not due to the assumed orientation of the methyl groups with respect to the ring, a series of calculations has been performed for the hexagonal conformation and for two distorted structures with $\rho = 0.020 \text{ \AA}$, $\varphi = 0^\circ$ and $\rho = 0.020 \text{ \AA}$, $\varphi = 180^\circ$. In these calculations several rotational orientations of the substituents have been considered. The results given in Table III show that the conclusion reached on the basis of Fig. 1 holds generally: for all rotational orientations of the methyl groups considered the quinoidal structure is the most stable and lies nearly 2000 cm^{-1} below the hexagonal form. The energy of the less-stable antiquinoidal and of the hexagonal structure shows somewhat larger variations with the methyl groups orientation, but considering the accuracy of the extrapolation, we cannot draw any conclusions. As we shall see later the effect on the wave function of the lowest triplet state is more pronounced.

The results of Table III refer to calculations for $\varphi = 0^\circ$ and 180° . It might be argued that the energy for $\varphi = 60^\circ$, 120° , 240° , or 300° could show a stronger dependence on the rotational orientation of the methyl groups. According to the arguments used in the past to explain the preference for certain values of φ the energy of the quinoidal conformation ($\rho = 0.020 \text{ \AA}$, $\varphi = 0^\circ$) should have been considerably affected by a rotation of the substituents. This is not observed, and we think it reasonable to assume that such arguments also are invalid for other values of φ . We conclude that in the lowest triplet state of p-xylene the quinoidal conformations are of lowest energy, irrespective of the rotational orientation of the methyl substituents with respect to the ring.

Some interesting observations are made by consideration of the results of the calculations for the conformations (b) of Table III. In Fig. 2(c) the orbital energies and the form of the π electron MOs are depicted for this case. Here the zx plane remains a plane of symmetry and the nodal structure of the benzene π electron structure is hereby fixed. As in Fig. 2(b) the orbital energies are shifted in accordance

with the electron repelling character of the methyl group. The virtual orbital associated with the antiquinoidal configuration is now higher in energy than the virtual orbital of the quinoidal one. As a result of the larger shifts in the occupied orbitals, however, the quinoidal configuration remains energetically more favorable.

In the population analyses for these conformations [see Table II(c)] we observe that the antiquinoidal side reveals the same behavior as in benzene, i.e., two allyl-like fragments are formed. In our calculations the influence of a rotation of the methyl groups on the energy of the lowest triplet state is limited. The situation that the energies remain about the same for two distinctly different population distributions resembles the effects encountered in the sudden polarization phenomenon.²⁷ It has been calculated that in that case the localization of the population lowers the energy, but the difference in energy with a delocalized description is very small.²⁸

A physical interpretation of the reason why the quinoidal minimum is stabilized with respect to the antiquinoidal minimum, irrespective of φ and rotational orientation of the methyl groups, is not easily given. In the past it was argued that the experimental results could be explained by considering the stabilization or destabilization effects of the methyl groups on the two types of radicals associated with the quinoidal and antiquinoidal conformations, but we have seen that this reasoning is contradicted by our calculations. In this context it is interesting to note the results of recent semiempirical calculations by Padma Malar and Jug on the lowest triplet state of a number of monosubstituted²⁹ and paradisubstituted³⁰ benzenes. According to their calculations the lowest triplet state of these molecules is always deformed to a quinoidal form, regardless of the electron attracting or repelling nature of the substituents. The reason for this behavior, according to these authors, should be looked for in "an interruption of the ring current by the substituents upon excitation." Such an explanation is supported by our calculations since for the lowest triplet state of p-xylene we find that the energy of the three possible quinoidal conformations hardly differs. Moreover, we have seen that the electronic structure in the lowest triplet state tends to the most localized structure, thus resisting a delocalization of the π electrons.

Vergragt, Kooter, and van der Waals¹⁵ have investigated the lowest triplet state of p-xylene in an isotopically mixed crystal by electron paramagnetic resonance experiments. They found that the electronic wave function of this state deviates considerably from D_{2h} symmetry, proving a distortion of the molecule which corresponds to a value of φ appreciably different from 0° or 180° . In particular, these EPR results revealed an unexpectedly anisotropic distribution of the spin density over the four unsubstituted carbon atoms. In terms of the numbering of Fig. 3: $\rho_i = \rho_i = 0.29$, $\rho_j = \rho_j < 0.11$ with $i = 2, j = 3$ or $i = 3, j = 2$. In the past it was believed that with the methyl group(s) in position(s) 1 (and 1') such a pronounced difference in spin density on the atoms 2 (2') and 3 (3') can only occur if the distortion is antiquinoidal with φ close to 60° or 300° in Fig. 3 (this corresponds to $\varphi = \pm 120^\circ$ using the conventions of Ref. 16).

TABLE III. Dependence of the energy (mH) of the lowest triplet state of p-xylene on the orientation of the two methyl groups. The zero of energy is defined as the energy of the lowest triplet state for the hexagonal conformation and methyl groups oriented as in (1). The axes system xyz is defined in Fig. 2.

Symmetry	$E(\rho = 0.02 \text{ \AA})$ $\varphi = 180^\circ$	$E(\rho = 0.00)$	$E(\rho = 0.02 \text{ \AA})$ $\varphi = 0^\circ$
(1) C_{2h} (C_2^x, σ_{yz})	-0.4	0.0	-7.7
(2) C_{2h} (C_2^y, σ_{zx})	-2.7	0.1	-7.6
(3) C_{2v} (C_2^x, σ_{zx})	-3.4	1.1	-7.5
(4) C_{2v} (C_2^y, σ_{yz})	-2.3	2.9	-6.5

When interpreting the EPR and microwave-induced delayed phosphorescence experiments on the isotopically mixed p-xylene crystal (and also those on aniline in a p-xylene host¹⁶) with a simple perturbation model developed for the π electron system of benzene,³¹ internal consistency of the data could be obtained for a structure close to, but not identical to, a pure antiquinoidal form. It is clear from the present work that this interpretation has to be revised; as the right-hand side of Fig. 3(b) shows, the inequality of the spin-density distribution on atoms 2 (2') and 3 (3'), most probably, arises from a skew quinoidal form.

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