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CONFORMATIONAL STUDIES ON ARYLCYCLOPROPANES—I

THE He–I PHOTOELECTRON SPECTRA OF α-ALKYL-PHENYLCYCLOPROPANES

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Abstract—The influence of α-alkyl substituents on the He–I photoelectron spectra of phenylcyclopropane, *p*-methoxy-phenylcyclopropane and *p*-chloro-phenylcyclopropane has been studied. From solution data (bulky) α-alkyl substituents are known to influence the relative orientation of the aryl and cyclopropyl groups and thereby their electronic interaction. In the photoelectron spectra however no significant influence of α-alkyl substituents on the position of the band attributable to ionization from the upper π levels of the aryl group is observed. These data seem to conflict with earlier reports about the gasphase conformation of the phenylcyclopropane system.

INTRODUCTION

Conjugative interaction between the cyclopropyl group and adjacent p- or π-electron systems has extensively been documented both from spectroscopic[1-12] and from thermodynamic[13-19] data.

Such interaction has generally been visualized in a semi-localized molecular orbital picture as the result of overlap between the π system and the two frontier Walsh-type orbitals[20] of the cyclopropane system denoted as e_a and e_a^* in Fig. 1.

For arylcyclopropanes maximum interaction between

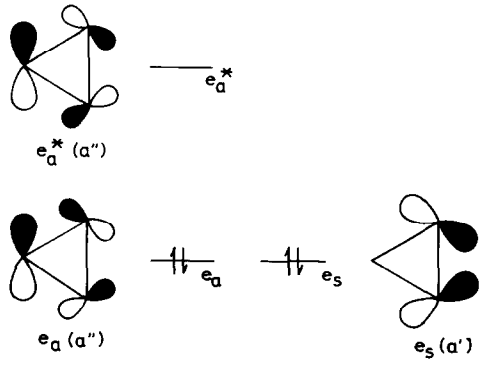


Fig. 1. The frontier Walsh-type orbitals of the cyclopropyl system, the symmetry labels refer to the C_s pointgroup.

the aryl π system and the cyclopropyl e_a and e_a^* orbitals[11,20] is achieved in the so-called bisected conformation (see Fig. 2) where the planes of the cyclopropyl ring and the aromatic system are perpendicular.

NMR spectroscopic studies of *p*-deuterophenylcyclopropane in CS_2 solution[2] revealed a temperature dependent shift for the *ortho* protons (see Fig. 2). This can be understood by assuming a rapid equilibrium between the bisected conformation, in which H_o is shielded by the magnetic anisotropy effect of the cyclopropane ring,[2] and the non-bisected conformation, in which this shielding effect is absent (see Fig. 2). At low temperature the bisected conformation was found to be favoured.

Recently Effenberger c.s.[11] concluded from NMR spectroscopic measurements that introduction of an α-Me group (R=Me, see Fig. 2) (i.e. in 1,3,5-tri(α-methyl)cyclopropylbenzene) leads to exclusive adoption of the non-bisected conformation, as a result of steric repulsion between R and H_o' (see Fig. 2) in the bisected conformation.

Gasphase electrondiffraction measurements on phenylcyclopropane have been reported[21] to indicate the exclusive presence of bisected molecules, while furthermore the energy difference between the first two bands in its He–I photoelectron spectrum (*vide infra*) has also been taken[12] as evidence for a preferred orientation with strong π-cyclopropyl interaction in the gasphase.

Thus it seemed worthwhile to study the influence of

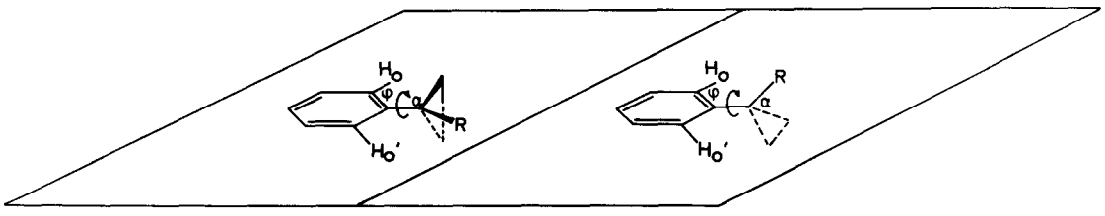


Fig. 2. The bisected (φ = 0°) and the non-bisected (φ = 90°) conformation of the arylcyclopropane system; φ is the dihedral angle between the plane of the aromatic system and the plane through C_1, C_α and R.

various α-alkyl groups (R) on the photoelectron spectra of phenylcyclopropanes, since any conformational changes induced, are expected to be accompanied by changes in the position of the electronic levels.

RESULTS AND DISCUSSION

Data about vertical ionization potentials measured for the systems studied by He-I photoelectron spectroscopy are compiled in Table 1, together with the data for some reference compounds. For three of these compounds—e.g. **1a**, **1b** and **1e**—the actual spectra are shown in Figs. 3–5.

The PE spectrum of **1a** has been reported earlier.[12] The first two bands (I_1 en I_2) in its spectrum can be attributed to ionization from orbitals which are mainly the highest π levels of the aromatic system.

The degeneracy of these orbitals is lifted as a result of overlap with the cyclopropane orbitals. The bands indicated by I_3 and I_4 can be attributed to ionization from levels which are mainly the upper Walsh type orbitals in character. Thus the distances between I_1 and I_2 and between I_3 and I_4 are expected to be rather sensitive for the relative orientation of the benzene and cyclopropane rings.

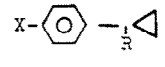
This idea is supported by the results of MIEHM (Modified Iterative Extended Hückel Method) calculations[24] (see Experimental) on the α-alkylphenycyclopropane system for various values of the dihedral angle ($\varphi = 0°$ for the bisected conformation; $\varphi = 90°$ for the fully non-bisected conformation). The splitting of the orbital energies calculated for the upper π-type levels and for the cyclopropane e-type levels are given as a function of φ for phenylcyclopropane in Fig. 6 and for α-Me-phenylcyclopropane in Fig. 7.

In both cases the splitting of the π levels is calculated to be about 0.4 eV larger for the bisected ($\varphi = 0°$) than for the non-bisected ($\varphi = 90°$) conformation.†

In contrast with expectations from the simple Walsh scheme presented in Fig. 1, a rather large π level splitting is predicted even for the non-bisected conformation. From an analysis of the MIEHM calculations it appears that for all values of φ the orbital identified as being mainly of the Walsh e_s-type (see Fig. 1) contains a rather

†Qualitatively INDO calculations gave the same results.[25]

Table 1. Vertical ionization potentials (eV) as determined by He-I photoelectron spectroscopy

Structure	I_1	I_2	I_3	I_4
Benzene[22]	9.23			
Toluene[23]	(8.9)	9.13		
Cumene[12]	8.98	9.20		
Cyclopropane[12]	10.90			
Methylcyclopropane[12]	10.10	10.90		
p-Methylanisole[22]	8.18	9.11		
p-Chlorotoluene[23]	8.90	9.57		
				
1a X=H R=H	8.66	9.21	10.53	11.11
1b R=Me	8.73	9.17	10.09	10.59
1c R=Et	8.70	9.17	9.95	10.50
1d R=Ipr	8.63	9.12	9.74	10.38
1e R=tBu	8.63	9.15	9.63	10.33
2a X=CH_3O R=H	8.05	9.08	10.13	10.67
2b R=Me	8.09	9.05	9.79	10.46
2c R=Et	8.11	9.02	9.69	10.31
2d R=Ipr	8.10	9.00	9.68	10.25
2e R=tBu	8.05	9.05	9.64	10.15
3a X=Cl R=H	8.64	9.47	10.49	10.98
3b R=Me	8.67	9.42	10.11	10.74
3c R=Et	8.64	9.42	10.04	10.61
3d R=Ipr	8.64	9.39	9.89	10.52
3e R=tBu	8.64	9.35	9.80	10.44

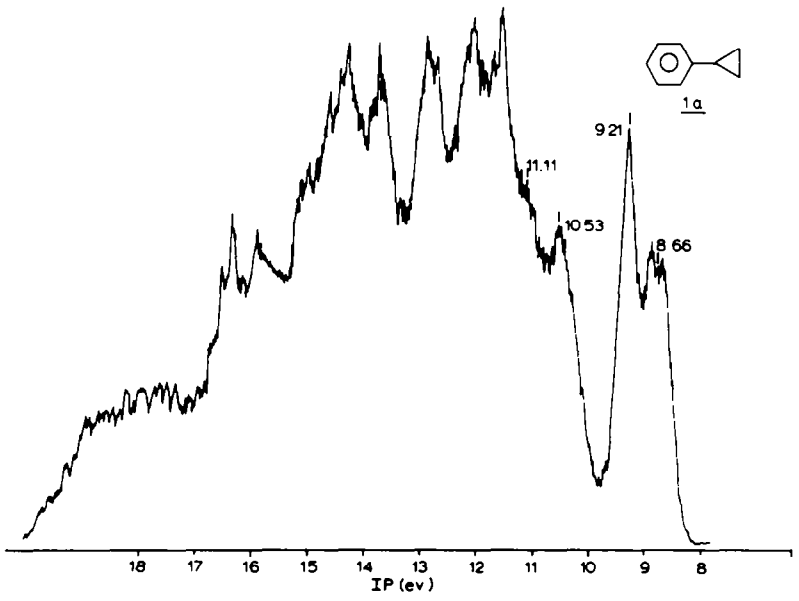


Fig. 3. PE spectrum of phenylcyclopropane (**1a**).

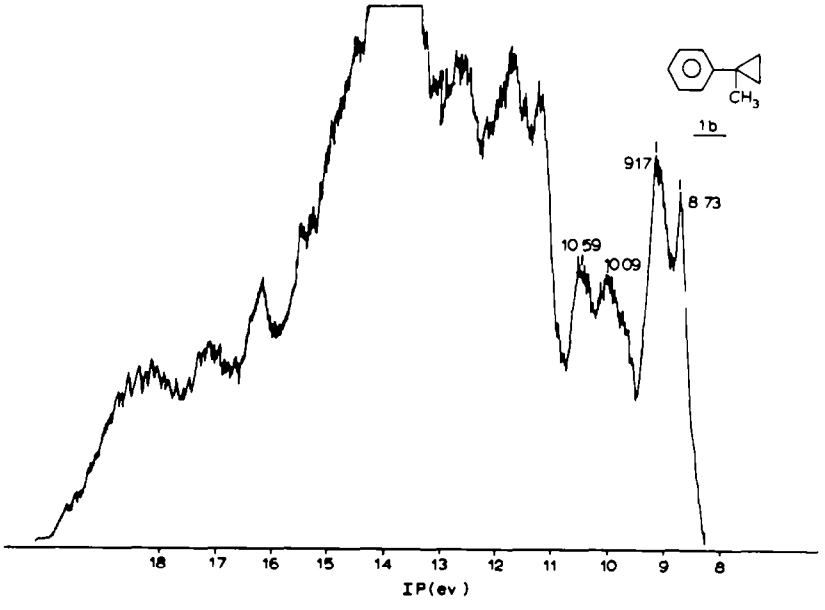


Fig. 4. PE spectrum of α-Me-phenylcyclopropane (**1b**).

large C-2p contribution in the cyclopropane ring-plane at the carbon atom connecting it to the phenyl ring.

Thus some interaction between a π system and the cyclopropane Walsh orbitals can even occur in a non-bisected conformation—as already pointed out by other authors[26,27]—which explains the π level splitting calculated for $\varphi = 90°$ (see Figs. 6 and 7).

From analysis of the data presented in Table 1 and Figs. 3–5 it is found that replacement of H_α by various alkyl groups has a destabilizing effect on the cyclopropane levels (I_3 and I_4) while the splitting of these levels remains almost constant at ~0.5 eV. No influence of R on the splitting nor on the position of the aromatic π levels (I_1 and I_2) is observed.

Introduction of a *para* substituent (X) in the aromatic system has the expected influence on the position and splitting of the upper π levels (I_1 and I_2) but no influence on the splitting of the cyclopropane levels (I_3 and I_4) and only a minor influence on their position.

From these observations it must be concluded that in *all* compounds studied little conjugation exists between the π MO's of the aromatic ring and the cyclopropane Walsh orbitals. Such a weak conjugation seems to point toward a non-bisected conformation for all compounds.

This conclusion is supported by our MIEHM calculations (see Figs. 6 and 7). For a non-bisected conformation these calculations predict that substitution of H_α by Me will hardly influence the splitting between I_3 and I_4 while also the I_1–I_2 splitting remains constant at about 0.5 eV, in accordance with the experimental observations.

For bulky R groups (e.g. R = Ipr, t-Bu) steric hindrance makes a non-bisected conformation the only plausible

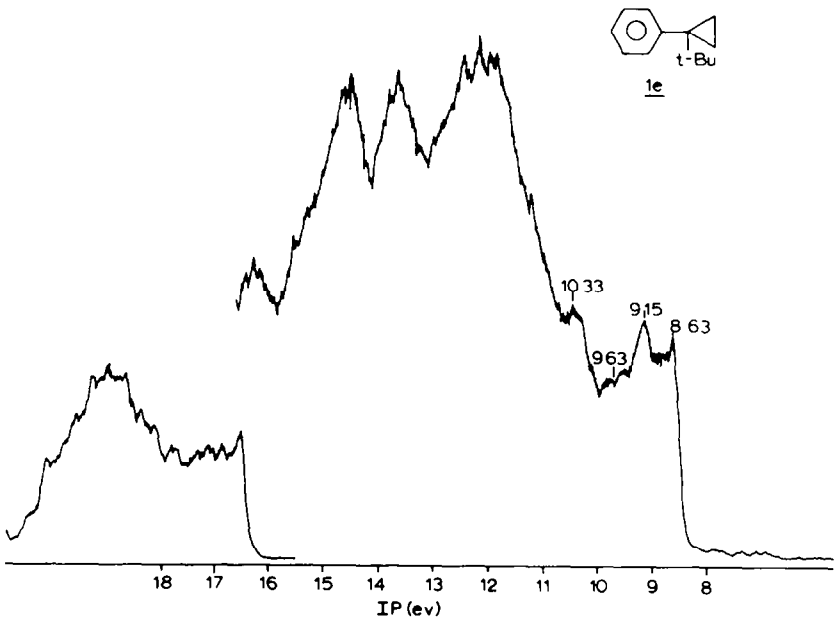


Fig. 5. PE spectrum of α-tBu-phenylcyclopropane (**1e**).

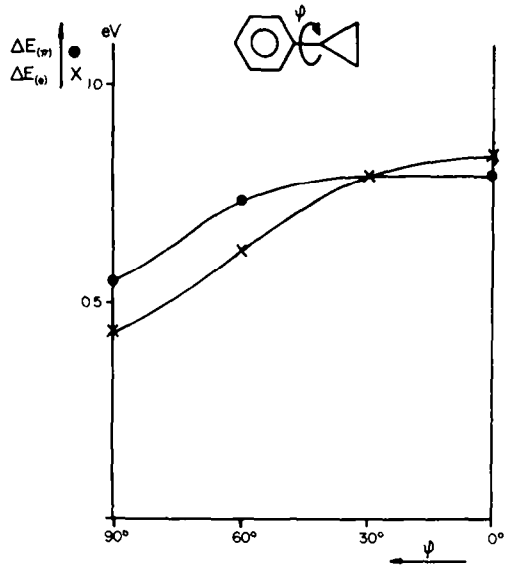


Fig. 6. Calculated splitting (MIEHM) of the upper π-type levels and the cyclopropane e-type levels as a function of φ in phenylcyclopropane.

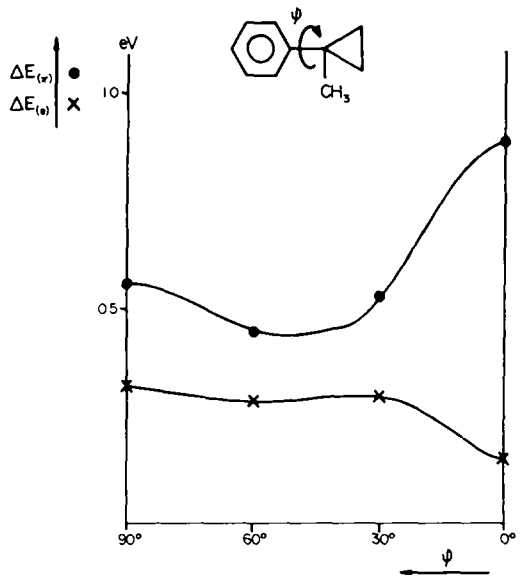


Fig. 7. Calculated splitting (MIEHM) of the upper π-type levels and the cyclopropane e-type levels as a function of φ in α-Me-phenylcyclopropane.

one; but especially for R=H this result seems quite remarkable in view of earlier reports[21] about the conformation of phenylcyclopropane in the gasphase.

EXPERIMENTAL

Phenylcyclopropane (**1a**) was obtained by pyrolysis of the pyrazoline formed by the reaction of cinnamaldehyde with hydrazine hydrate.[28] Compounds **1b**, **1c**, **1d** and **1e** were obtained via a modified Makosza catalysis in the addition of dichlorocarbene to the olefinic bond.[29]

The same procedure was followed in the synthesis of the *p*-MeO compounds. The *p*-Cl compounds were prepared by chlorination of the appropriate phenylcyclopropanes, using $FeCl_3$ as a catalyst for R = Me, Et, Ipr and t-Bu.[30]

All samples were purified by GLC on a Varian Aerograph, model 90-P, using a SE 30 column. Identification of the compounds was done by means of IR and NMR spectroscopy.

The photoelectron spectra (Resolution 0.02 eV) were recorded on a Vacuum Generators type ESCA spectrometer employing He–I emission (21.21 eV) as the ionizing radiation. Calibration was achieved by the use of Ar as an internal reference.

Calculations of the orbital energies of the phenylcyclopropane and the α-Me-phenylcyclopropane system were carried out following the MIEHM method, developed by Larsen.[24]

The coordinates of the phenylcyclopropane system were determined using the following geometry parameters:[21] bondlengths: C–C (benzene) 1.40 Å, C–C (all others) 1.50 Å, C–H 1.08 Å; angles: HCH (cyclopropane) 120° and 128.5° for the angle between the plane of the cyclopropane ring and the bond connecting it to the benzene system.

For the α-Me-phenylcyclopropane system the same coordinates were used, while the bondangles within the methyl group were chosen to be 109.5°.

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