HeI Photoelectron Studies of Unstable Ketenes: Mono- and Di-phenylketenes, and their Gas-phase Conformations

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HeI photoelectron spectra are reported for the semistable mono- and di-phenylketene molecules generated in high yield by *in situ* metal dehalogenation reactions of the appropriate chlorophenyl-substituted acid chlorides. The photoelectron results can be interpreted through a simple perturbation approach, and in conjunction with semiempirical MNDO and AM1 calculations provide gas-phase structural evidence for a planar π-conjugated monophenylketene molecule, and a non-planar diphenylketene species in which both phenyl groups are rotated, in a conrotatory fashion, some 30–40° out of the $>C=C=O$ π system. The limitations of the MNDO method and the greater reliability of AM1 for the assessment of the relative energies of rotational conformers is discussed. HAM/3 calculations are in excellent agreement with the experimental ionisation potentials.

Ketene and substituted ketenes are unstable molecules which easily undergo cycloaddition reactions to form alkenes and other unsaturated molecules.[1,2] They are thus generally prepared *in situ* for solution reactions, mainly by dehalogenation or dehydrohalogenation reactions. The few attempts that have been made to synthesise discrete substituted ketenes in solution have failed, since the formation of the dimer, in one form or another, is more favourable.[3] The generation of gas-phase ketenes for spectroscopic observation with a view to investigation of electronic and geometric properties, has generally involved an extension of the solution procedures. Thus a series of mono- and di-substituted ketenes involving Cl, Br, CH_3, and CN substitution have been generated and studied by a variety of gas-phase techniques, including ultraviolet photoelectron spectroscopy (UVPES).[4–8] These results have provided, through an analysis of the orbital energies, an indication of the extent of interaction of the substituent with the $>C=C=O$ π system.

Substitution by a phenyl group is expected to confer some additional stability on the molecule by virtue of π conjugation, although it is also anticipated that steric interactions in the diphenyl case due to H atoms on adjacent rings, will lead to non-planarity and a loss of this conjugation. Nevertheless, the use of phenylketenes in solution reactions, particularly for [2 + 2] and [4 + 2] cycloadditions, is widespread,[9–11] and an explicit synthesis for diphenylketene has been reported.[12,13] Monophenylketene has not, however, been isolated due to its propensity to polymerise.[14]

It is the intent of this work to demonstrate that mono- and di-phenylketene (MPK and DPK) can be generated essentially quantitatively in the gas phase, observed by photoelectron spectroscopy (PES), and their conformations evaluated by investigation of the π-orbital distributions in conjunction with semiempirical calculations involving the MNDO and AM1 Hamiltonians. This is especially relevant in the context of the gas-phase structures of the analogous ethylenic molecules where considerable attempts have been made over the years to establish conformations of the free molecules. It seems clear now that the monophenyl species, styrene, is planar,[15–19] whereas diphenyl substituted species, *e.g.* 1,1-diphenylethylene,[16–19] and indeed, benzophenone,[20–24] are non-planar, although many discrepancies in the experimental and theoretical studies remain. The main issues, as with the phenyl substituted ketenes discussed here, involve the degree of non-planarity reflected in the torsional angle(s) θ (and θ'), the relative orientation of the phenyl groups, and the ability of semiempirical methods to locate these structures. In the past the MNDO method has performed poorly for rotation about a single bond due to an overestimation of non-bonded repulsions, whereas the more recent AM1 method[25] corrects some of these defects.[26–29]

Experimental

Monophenylketene was generated by gas-phase dehalogenation of (±)-2-chloro-2-phenylacetyl chloride (Aldrich) using mossy zinc packed loosely into a 25 cm quartz tube. The starting material was raised to 50 °C to achieve sufficient vapour pressure, and the zinc was maintained at 250 °C.

Diphenylketene was prepared *in situ* by an analogous dehalogenation procedure using zinc at 250 °C; the starting material was 2-chloro-2,2-diphenylacetyl chloride (Aldrich) heated to 50 °C. Since DPK is more stable than MPK, a specific synthesis was also effected involving dehydrohalogenation of diphenylacetyl chloride with triethylamine in diethyl ether at 0 °C.[13] An orange solid, which could be kept for several weeks at −20 °C, showed an intense infrared band at 2 098 cm^{-1} characteristic of all ketenes,[30] in agreement with a literature solution value.[31] This material gave identical PE spectra to those obtained from the *in situ* method.

The gaseous effluent from the pyrolysis reactions was pumped directly into a PE spectrometer designed for the study of transient and unstable molecules.[32] Resolution was 40 meV under the conditions of the experiment, and spectra were calibrated using the known ionisation potentials (E_i) of CO, CH_3I, and Ar.

Semiempirical calculations were performed on VAX 11/785 and 8 800 computers using the standard MOPAC[33] and AMPAC[25] programs. In general, the molecular structures were allowed to optimise freely within the constraints of, say, planar, or twisted structures (see below). However, intra-ring bond lengths *e.g.*, C–C and C–H, and intra-ring angles were maintained to be equal; this does imply that a completely refined optimisation would lower the calculated heats of formation by a small margin, although this was tested, and did not change the relative magnitudes of the results.

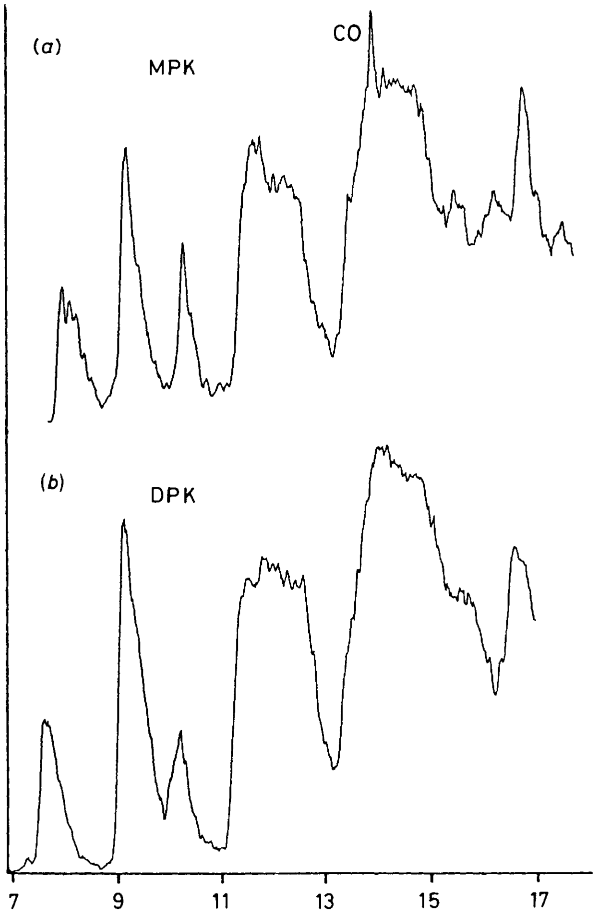

Figure 1. HeI photoelectron spectrum for (*a*) monophenylketene (MPK), and (*b*) diphenylketene (DPK).

Table. Vertical ionisation potentials (eV) for monophenyl- (MPK) and diphenylketene (DPK).

MPK[a]	DPK[a]
8.06 (2 250 ± 60 cm^{-1})[b]	7.64
9.31	9.18
10.39	10.19
11.77	11.64
12.36	12.1
13.6 (sh)	13.5 (sh)
14.5	14.1
15.62	14.7
16.34	15.64
16.86	16.68

[a] First three E_is, ±0.02 eV; the rest, ±0.05, and ±0.1 eV. [b] Vibrational structure observed on first band.

Results

The HeI photoelectron spectra of MPK and DPK are shown in Figure 1, and can be assigned to the spectra of these molecules by comparison with known data for the parent ketene molecule,[34] and the analogous ethylenic molecules for which PE spectra are available.[19] A trace of CO (peak at 14.0 eV) is evident in the spectrum of MPK, which increases as the temperature is raised further; indeed experiments involving higher temperature pyrolysis of both of these species indicate the possible intermediacy of carbenes as noted previously for the halo-substituted ketenes.[8] The measured vertical values of E_i are given in the Table.

Discussion

The low E_i region (7–11 eV) in both molecules provides the key to any discussion regarding conformations and orbital assignments, since it is here that the highest lying π-molecular orbitals (MOs) will maintain sensitivity to any coupling, and uncoupling (by torsion), of the phenyl and $>C=C=O$ π systems.

Conformations.—In the MPK case, which is the easiest to treat, the ketene substitution splits the benzene e_{1g} degeneracy at 9.25 eV,[35] and two phenyl based π orbitals result. One of these has a node at the point of substitution, and remains relatively unchanged in position; the other can interact with the $>C=C=O$ non-bonding π orbital (9.63 eV in the parent ketene molecule[34]), leading to the overall formation of three bands below 11 eV. The first (π_5) and third (π_3) separate away from the 9.25 eV median (π_4) as the π coupling becomes more pronounced; the large experimentally observed separation of $E_i(1)$ and $E_i(3)$ is indicative of considerable conjugation, and hence a planar (C_s), or close to planar, structure for this molecule.

The distribution of these three values of E_i, roughly every 1.1 eV, can be followed (assuming Koopmans' theorem) by the semiempirical calculations as illustrated in Figure 2 which shows calculated values of E_i up to 13 eV using MNDO and AM1 for three possible optimised conformations; a planar structure ($\theta = 0°$), a perpendicular structure ($\theta = 90°$), and one in which the phenyl group has been allowed to rotate freely until a minimum in energy was obtained.

Three features emerge from Figure 2, which also shows, in the lower half, the calculated heats of formation (ΔH_f) at each conformation. Firstly, as a general comment, AM1 consistently calculates ΔH_f values a few kJ mol^{-1} higher than MNDO; this seems to be a feature of the method which generally gives calculated values closer to experiment.[25] In addition, E_i (for the same structure) are a little higher by AM1 than by MNDO for this class of compound although, in general, AM1 gives improved first E_i.[25] Secondly, the MNDO surface is extremely flat with 1.3 kJ mol^{-1} spanning all three conformations, and a minimum found at a twist angle (θ) of 58.2°, with the perpendicular structure at an essentially identical energy. This is undoubtedly an artifact of the method, and simply represents the well known tendency of MNDO to overestimate torsional angles; clearly the MNDO orbital energies for the planar structure are much more in keeping with the experimental values, which are also shown in Figure 2. Thirdly, AM1, gives a result entirely in keeping with experiment; the perpendicular structure is destabilised (albeit by only 8.4 kJ mol^{-1}), and the found minimum structure (Figure 3) corresponds to a planar C_s conformation, and the most reasonable distribution of calculated E_i. This distribution is analogous to that found in styrene, a molecule that has been demonstrated recently to be planar.[18]

The addition of a second phenyl group, which may be treated as a perturbation on MPK, leads to increasing complexity in the PE spectrum of DPK (Figure 1). Nominally, three bands are observed below 11 eV, although the second, from its intensity and broadness corresponds to three E_i values. These first five E_i values correspond to the π levels, π_8, (π_7, π_6, π_5) and π_4, with the separation between π_8 and π_4 reflecting the extent of the interaction between the $>C=C=O$ and aromatic fragments described by the resonance integral, $\beta = \langle\psi_{C=C=O}|H|\psi_A\rangle$. β will be modified by the usual cos θ dependency according to $\beta_\theta = \beta\cos\theta$. Solution of the secular determinants[19] leads to equation (1) where ΔI corresponds to the experimental energy

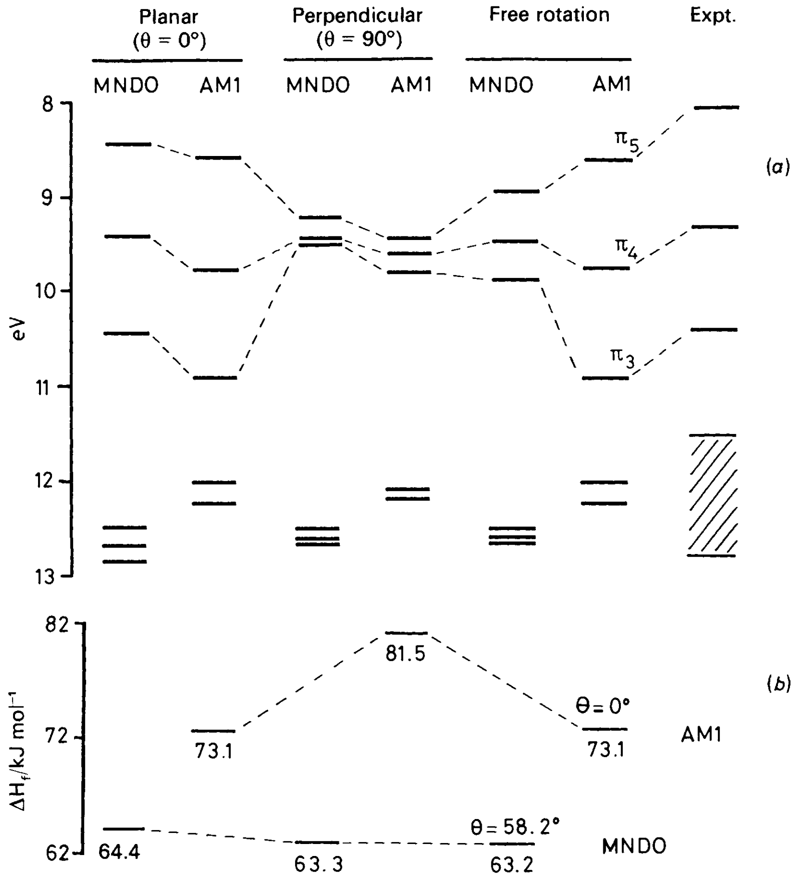

Figure 2. Comparison of the calculated orbital energies (*a*) of MPK (eV), and the corresponding ΔH_f values (*b*) (kJ mol^{-1}) with experiment using MNDO and AM1 at two fixed structures (phenyl group planar, or perpendicular with respect to the (H)CCO plane), and one in which the phenyl group is free to rotate to a minimum in energy.

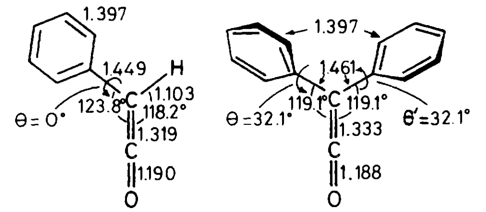

Figure 3. Optimised structures by AM1 for MPK and DPK, leading to C_s and C_2 conformations, respectively. Note that inter-ring bond lengths and bond angles were constrained to be equal. All other parameters including θ and θ′ were allowed to optimise.

difference ($\pi_5 - \pi_3$ in MPK, and $\pi_8 - \pi_4$ in DPK), and $M = 4$ and 8 for mono- and di-phenyl-substituted species, respectively. The basis orbital energies for the $>$C=C=O ($A_{C=C=O}$) and phenyl fragments (A_2) within this LCMO scheme can be obtained from values for substituted ketenes and styrene, respectively, thereby separating the electronic and steric effects. Assuming that methyl substitution on ketene

$$\cos\theta = \left[\frac{\Delta I^2 - (A_{C=C=O} - A_2)^2}{M\beta^2}\right]^{\frac{1}{2}} \qquad (1)$$

produces a similar shift to that of a phenyl group, values from known data on methylketenes[7] can be used. A working value of β (1.15 eV) is obtained from the reasonable assumption that MPK is planar, and this can then be used to determine a value for the twist angle in DPK.* This leads to a value of 43°, in close agreement with a similar analysis for 1,1-diphenylethylene.[19] This simple first-order perturbation analysis neglects any second-order effects, *e.g.* σ/π mixing, and probably leads to an upper estimate for the torsional angle from the use of the methylketene values for the $A_{C=C=O}$ basis orbital energy.

Both the MNDO and AM1 calculations confirm this prediction, with high-energy planar structures, and lower-energy twisted structures [Figure 4(*b*)]. However, as in the case of similar calculations on benzophenone,[21] MNDO badly overestimates the angles of the twisted structure, with a minimum found at θ = θ′ = 90° (both phenyl groups perpendicular), and an energetically close structure (1.5 kJ mol^{-1}) with angles of θ = 53.9 and θ′ = 71.3°. The former leads to a poor (bunched) distribution of E_i values, with the latter beginning to approach the experimental spread. AM1 on the other hand predicts the most stable structure with equal twist angles of 32.1° in a conrotatory (or helical) fashion, and hence a C_2 structure (Figure 3), which corresponds closely to the most recent data on benzophenone.[23] The distribution of calculated E_i from this structure up to 13 eV [Figure 4(*a*)] is, therefore, in good qualitative agreement with the experimental spectrum, although with the usual shift to high energy. Interestingly, a proposed conformation for benzophenone in which one phenyl ring is planar to the $>$C=O and the other is twisted by a large angle,[20] turns out to be also very close in energy for DPK using AM1 (1.9 kJ mol^{-1}, θ′ = 90°), but not quite so close (9.0 kJ mol^{-1}) by MNDO. In fact, at the AM1 level, with one phenyl held planar (θ = 0°) and the other allowed to optimise, a comparable structure with θ′ = 70.4° is obtained with a ΔH_f value (196.1 kJ mol^{-1}) between the two lowest-energy struc-

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* This assumes that β is invariant to any small change in bond length incurred by twisting.

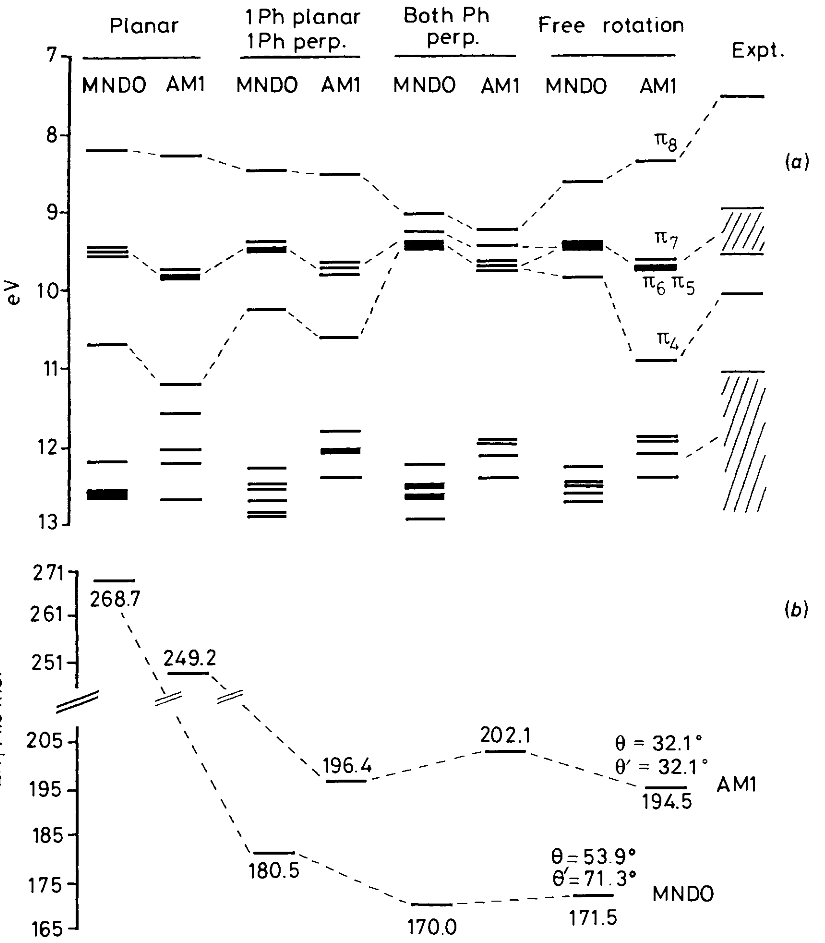

Figure 4. Comparison of the calculated orbital energies (*a*) of DPK (eV), and the corresponding ΔH_f values (*b*) (kJ mol^{-1}) with experiment using MNDO and AM1 at three fixed structures (both phenyl groups planar, 1 planar/1 perpendicular, or both perpendicular to the (C)(C)CCO plane), and one in which both phenyl groups are free to rotate to a minimum in energy.

tures; clearly the surface for rotation of one phenyl group is very flat when the other phenyl group is held perpendicular. Nevertheless, the match of values of experimental and theoretical E_i indicates that the found minimum structure, with equal twist angles, is the most reasonable.

Assignments and Calculated Orbital Energies.—Monophenylketene. The first band with coincident adiabatic and vertical E_i of 8.06 eV, has a Franck–Condon envelope reminiscent of the π_{nb} orbitals observed in all substituted ketenes,[8] with a primary vibrational progression of 2 250 cm^{-1}, corresponding to a slightly increased CCO symmetric stretching frequency. The position of this band and its counterpart at 10.39 eV which separate away from the purely benzene π region (at 9.3 eV) is mimicked fairly well by the calculations.

However, there are notable differences between the MNDO and AM1 methods which become more apparent for the higher E_i values. Both methods tend to calculate values that are too high, and this discrepancy worsens for the higher E_i. As already noted, AM1 seems to exaggerate this trend in that the first three distinct E_i are each calculated from 0.2 to 0.5 eV higher than the MNDO values. In addition, above 11 eV the experimental spectrum shows a broad band extending to 13 eV, and the planar MNDO and AM1 results differ significantly as to whether there are three (MNDO) or two (AM1) bands in this region. The AM1 method prefers a stabilisation of the π orbital and an assignment into the next group of bands above 15 eV. This is probably erroneous given that π_1 in benzene is known to occur at 12.1 eV; AM1 results for benzene[25] accordingly predict the $1a_{2u}$ orbital to be excessively stabilised. To investigate this further and thoroughly, at the *ab initio* level would require an extravagant use of cpu time and the continued reliance on Koopmans' theorem. An alternative procedure, HAM/3,[36] which although parametrised with known E_i (including those of benzene and ketene), uses a half-electron method for calculating E_i, and has been demonstrated to be remarkably accurate in the calculation of values of E_i for unstable, and hence unparametrised, molecules.[37] Since the program involves no second derivative evaluation, E_i values were calculated for MPK and DPK at the optimised AM1 geometries (Figure 3). The results are shown in Figures 5 and 6 which compare eigenvalues from all three computational methods to the experimental results for both molecules.

It is clear that HAM/3 performs remarkably well, especially for the first three bands of each molecule, and the clustering distribution of the E_i values all the way up to the distinct sharp pσ orbital in each molecule at 16.7–16.9 eV. This is in contrast with the aforementioned tendency of both MNDO and AM1 to more evenly distribute the higher values of E_i, in addition to calculating them too high. The result confirms that the 11–13 eV region of MPK contains three E_is, including π_2, in accord with MNDO (Figure 5).

Above 13.5 eV there are many E_i values clustered together and specific assignments will not be attempted, although HAM/3 does show reasonable groupings, and accurately predicts the position of the pσ orbital at 16.9 eV; this band has

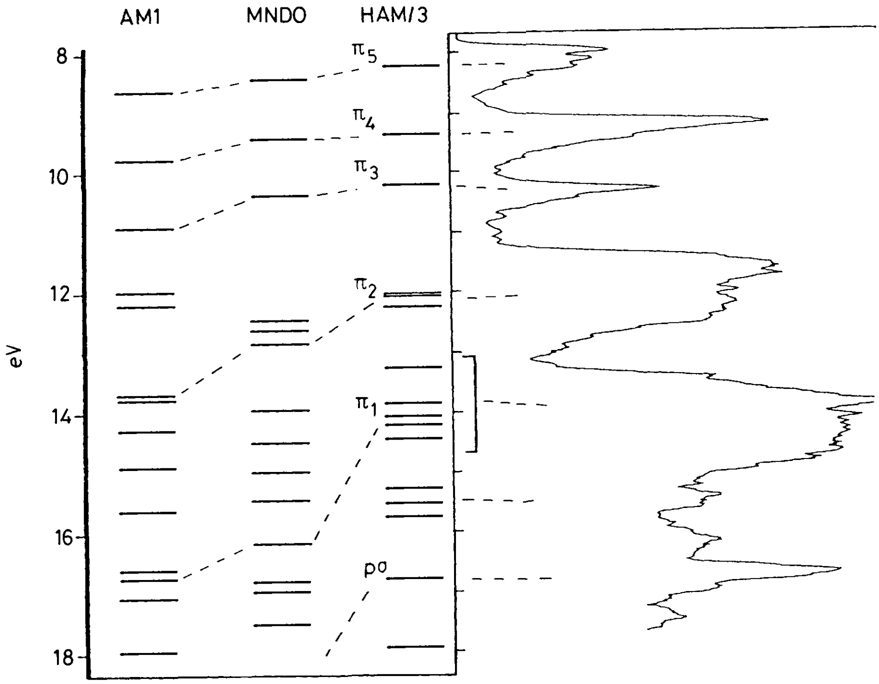

Figure 5. AM1, MNDO, and HAM/3 calculations for MPK at the optimised (AM1) structure (Figure 3); comparison with experiment. Orbitals identified as π are labelled.

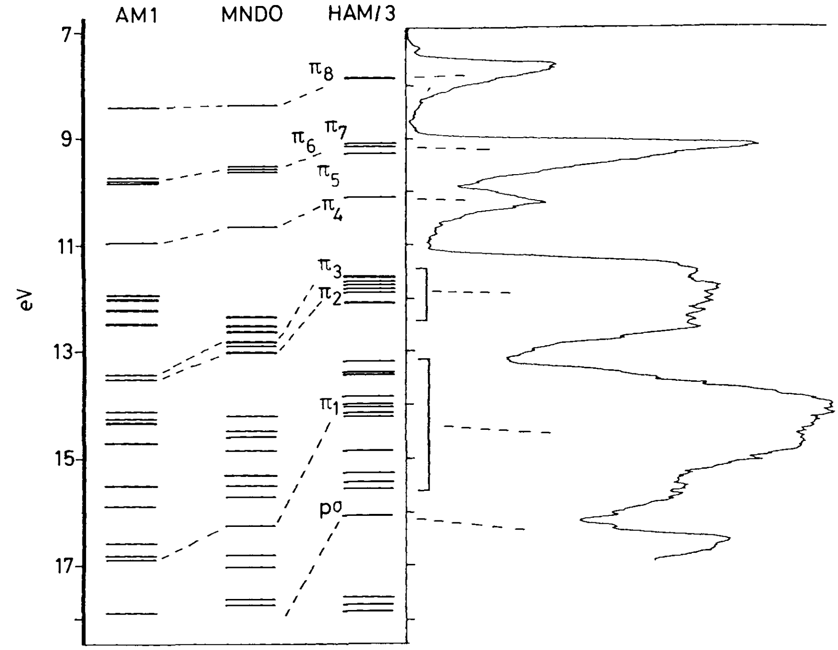

Figure 6. AM1, MNDO, and HAM/3 calculations for DPK at the optimised (AM1) structure (Figure 3); comparison with experiment. Orbitals identified as π (with respect to the individual phenyl planes) are labelled.

been noted before[8] as a unique feature in the spectra of all ketenes.

Diphenylketene. The first band shows no resolvable vibrational structure, but has coincident adiabatic and vertical E_is at 7.64 eV. The destabilisation, with respect to the corresponding band in MPK, overcomes the loss of conjugation, a feature reminiscent of the styrene–1,1-diphenylethylene pair.[19] Similar comments to those discussed above hold for the AM1 and MNDO calculations (Figure 6), although the 2.55 eV experimental separation between π_8 and π_4 (referring to orbitals out of the plane of the twisted phenyl rings) is matched fairly well by all three calculations. The HAM/3 calculation, at the optimised AM1 geometry, is clearly superior, accurately pin-pointing these high lying MOs. It should also be remarked that the MNDO calculations were also performed at the optimised AM1 geometry ($\theta = \theta' = 32°$), and show a superior agreement with experiment. The MNDO ΔH_f value at this geometry (206.7 kJ mol^{-1}) has, however, started to rise as non-bonded interactions begin to dominate.

AM1 and MNDO again show differences for the next group of bands between 11 and 13 eV with, respectively, four and six E_is predicted and AM1 stabilising the π levels; HAM/3 shows a tight cluster of six E_is in agreement with MNDO. Once more, above 13 eV, specific assignments cannot be established apart from the distinctive presence of the pσ orbital at 16.68 eV, well predicted by HAM/3 (Figure 6).

Conclusions

The HeI photoelectron spectra of the semistable molecules MPK and DPK are reported, and on the basis of semiempirical (in particular AM1) calculations, and the distribution of E_i it is apparent that MPK is planar and DPK is not. The potential surfaces for torsion of the phenyl (MPK), or a single phenyl ring with the other held perpendicular (DPK) are relatively flat. A first-order perturbation analysis indicates twist angles of 43° for DPK, compared with calculated (AM1) values of 32.1°. Clearly, the choice of basis orbital energies is important in estimating the extent of non-planarity in DPK; the estimated values thus have a wide margin of error (estimated to be ±10°), but are nonetheless consistent with the substantial number of results on benzophenone and 1,1-diphenylethylene. Also it is clear that AM1 is superior to MNDO for such structural problems, although it should be borne in mind that there are some well established difficulties in the ability of MNDO and AM1 to reproducibly map out conformational hypersurfaces.[38] Finally, given the lack of *ab initio* effort in this area, and the poor performance of AM1 for π-bonding levels, it would seem that the semiempirical HAM/3 method provides the best estimate of the experimental orbital energies.

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