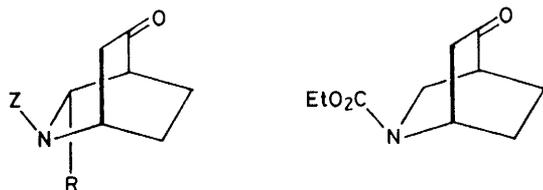


## Photoelectron Spectroscopic Studies of Some 2-Azabicyclo[2.2.2]octan-5-one and Bicyclo[2.2.2]octanone Derivatives

By Frank Carnovale, Tiang-Hong Gan, and J. Barrie Peel,\* Department of Physical Chemistry and Research Centre for Electron Spectroscopy, La Trobe University, Bundoora, Victoria 3083, Australia  
Andrew B. Holmes,\* University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

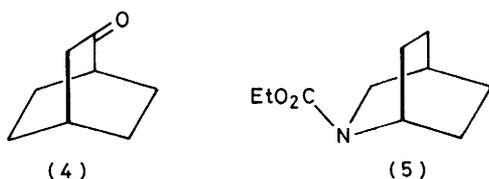
The He<sup>I</sup> photoelectron spectra of several 2-ethoxycarbonyl-2-azabicyclo[2.2.2]octane and bicyclo[2.2.2]octanone derivatives have been measured. The low ionization potentials of these compounds are well characterised by comparison with the results of HAM/3 molecular orbital calculations. In particular, a significant interaction is observed between the nitrogen lone-pair and the carbonyl oxygen at C-5 of 2-ethoxycarbonyl-2-azabicyclo[2.2.2]octan-5-one

DURING our studies on the synthesis of prosopine we investigated the Baeyer–Villiger oxidation of the azabicyclo[2.2.2]octanones (1) and (2).<sup>1</sup> We<sup>2</sup> and others<sup>3</sup> subsequently extended these investigations to include the unsubstituted ketone (3). In order to evaluate the possible existence of an electronic interaction between the nitrogen and the carbonyl group at C-5 in such azabicyclo-octanones we initiated a photoelectron spectroscopic study, which is reported in the present paper.



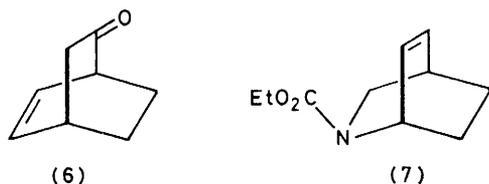
(1) R = CO<sub>2</sub>Me, Z = PhCH<sub>2</sub>OCO  
(2) R = CH<sub>2</sub>OCOPh, Z = PhCH<sub>2</sub>OCO

(3)



(4)

(5)



(6)

(7)

Photoelectron (p.e.) spectroscopy, particularly using the He<sup>I</sup> (21.22 eV) ionization source, is now well established as a technique for structural studies of organic molecules in the vapour state. For large molecules p.e. spectroscopic studies generally concentrate on those ionization bands associated with specific electronic features of the structure. These include the  $\pi$  and  $n$  orbitals which are mostly found in the low ionization potential (IP) region. Analysis of IP shifts in bands of related molecules leads to quantitative data describing

the inductive and resonance effects operating in such systems.<sup>4</sup> In particular cases, the degree of conjugation, both homoconjugative and hyperconjugative, can be estimated.<sup>5</sup>

Morishima *et al.*<sup>6</sup> have obtained IP data in a study of non-adjacent  $n,\pi$  electronic interactions in unsaturated derivatives of five- and six-membered cyclic and bicyclic amines. The bishomoallyl homoconjugation in five-membered amines favours  $n,\pi$  through-space interaction with destabilization of the lone-pair,  $n_N$  orbital, whereas the homoallyl conjugation in six-membered amines involves  $n,\pi$  and  $\pi,\pi^*$  interactions with a little stabilization or destabilization of the lone-pair orbital.

Comparisons between some 2-azabicyclo[2.2.2]octanes and their related 2-azabicyclo[2.2.2]oct-5-enes show 0.1–0.2 eV stabilization of the  $n_N$  IP in the unsaturated octene compounds. This indicates that the orientation of the nitrogen lone-pair does not allow resonant interaction with the  $\pi$  orbital, the observed stabilization thus resulting from the general decrease in CH hyperconjugation.<sup>6</sup>

Earlier p.e. studies of bicyclic hydrocarbons and related systems include work on norbornane, norbornene, norbornadiene, and the corresponding bicyclo[2.2.2]octanes by Bischof *et al.*,<sup>7</sup> the norbornanones and norbornenones by Chadwick *et al.*,<sup>8</sup> isopropylidene-norbornane, -norbornene, and -norbornadiene by Heilbronner and Martin,<sup>9</sup> and 2,3-diazabicyclo[2.2.*n*]alk-2-enes by Boyd *et al.*<sup>10</sup>

In examining the possible long-range  $n_N-n_O$  interactions in 2-ethoxycarbonyl-2-azabicyclo[2.2.2]octan-5-one (3) the present He<sup>I</sup> p.e. study includes measurements on the related molecules bicyclo[2.2.2]octan-2-one (4), 2-ethoxycarbonyl-2-azabicyclo[2.2.2]octane (5), bicyclo[2.2.2]oct-5-en-2-one (6), and 2-ethoxycarbonyl-2-azabicyclo[2.2.2]oct-5-ene (7).

### EXPERIMENTAL

The carbocyclic ketones (4) and (6) were prepared as described by Freeman *et al.*,<sup>11</sup> while the azabicyclo-octene (7) and its saturated derivative (5) were prepared following the method of Cava.<sup>12</sup> The azabicyclo-octanone (3) was prepared according to the method of Krow.<sup>13</sup>

The p.e. spectra were measured on a double-chamber instrument<sup>14</sup> with some samples requiring the use of a resistively heated glass inlet system to provide the necessary

vapour pressure. Time-averaged He<sup>I</sup> spectra of 512 points were obtained over 2 h periods at maximum count-rates of *ca.* 1 000 s<sup>-1</sup> and at an operational resolution of *ca.* 35 meV. Calibration was achieved using an acetylene–nitrogen mixture with each sample. The spectra are shown in Figure 1.

The general features of each spectrum are the well defined low IP bands in the 8–11 eV range with overlapping hydrocarbon bands in three groups dominating the 11–18 eV range. It is convenient to confine the analysis of the spectra to the low IP range, so the vertical IPs below 11.5

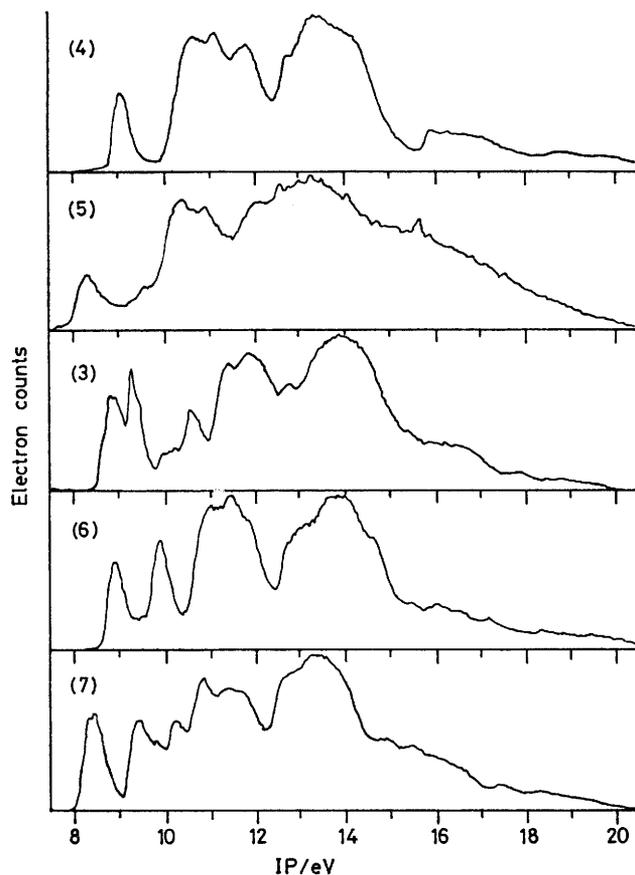


Figure 1 He<sup>I</sup> P.e. spectra in (3)–(7)

eV for each of the five molecules are listed in the Table where they are given orbital assignments derived with the assistance of calculated data which are also listed.

#### CALCULATIONS

Based on the validity of the Koopmans' approximation, numerous semi-empirical and *ab initio* MO methods have been used to derive assignments for p.e. spectra.

The substituted bicyclo-octanes are of such a size that only semi-empirical calculations can be performed with convenience. We have used the HAM/3 method recently developed by Lindholm and his co-workers.<sup>15</sup> This method has been shown to give good predicted IPs for various organic molecules.<sup>16–18</sup>

Molecular geometries were based on standard bond lengths and the only conformational variations considered were associated with the nitrogen atom in the ring and the associated urethane ethoxycarbonyl group attached to it.

It is likely that the nitrogen atom has a planar rather than

pyramidal disposition of the three N–C bonds, and there are considerable differences in the HAM/3 IPs for such different structures. For instance, the first IP of the saturated azabicyclo-octane (5) at 8.43 eV and associated with the

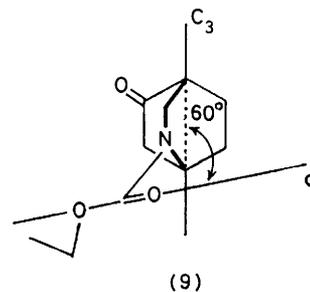
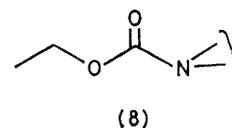
Comparison of experimental and calculated vertical ionization potentials for some substituted bicyclo[2.2.2]-octanones (in eV)

(4)			(5)		
IP <sup>a</sup>	MO	–ε <sup>b</sup>	IP <sup>a</sup>	MO <sup>c</sup>	–ε <sup>b</sup>
9.07	n <sub>O</sub>	9.10	8.43	n <sub>N</sub>	8.68
10.77		10.87	9.67	n <sub>O'</sub>	9.86
11.26		11.02	10.50	π* <sub>OO</sub>	10.63
			11.03		10.77
(3)			(6)		
IP <sup>a</sup>	MO <sup>c</sup>	–ε <sup>b</sup>	IP <sup>a</sup>	MO	–ε <sup>b</sup>
8.89	n <sub>N</sub> – λn <sub>O</sub>	8.90	8.96	n <sub>O</sub>	9.11
9.29	n <sub>O</sub> + λn <sub>N</sub>	9.18	9.89	π <sub>CC</sub>	9.84
10.12	n <sub>O'</sub>	10.04	10.91		10.94
10.65	π* <sub>OO</sub>	10.74			
11.40		11.36			
(7)					
IP <sup>a</sup>	MO <sup>c</sup>	–ε <sup>b</sup>			
8.52	n <sub>N</sub>	8.68			
9.47	π <sub>CC</sub>	9.45			
9.91	n <sub>O'</sub>	9.88			
10.34	π* <sub>OO</sub>	10.63			
10.91		11.00			

<sup>a</sup> Accuracy is *ca.* ±0.05 eV. <sup>b</sup> HAM/3 calculated IPs. <sup>c</sup> n<sub>O'</sub> and π\*<sub>OO</sub> are localized in the OCO group.

nitrogen non-bonding n<sub>N</sub> orbital is calculated at 8.68 eV in the favoured planar arrangement, but is never lower than 9.08 eV for the numerous geometries used with a pyramidal nitrogen atom. Consequently the planar disposition of the nitrogen atom is indicated for the three molecules in the present study.

The conformation of the urethane ethoxycarbonyl group has a lesser influence on the calculated HAM/3 IPs but an open staggered geometry (8) gave generally better results. Rotation about the N–C bond caused steady variations in the low IPs of each of the three molecules considered. While the maximum variation of any IP was 0.4 eV, the

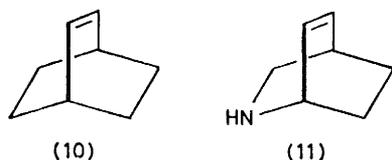


molecular orbital compositions remained fairly constant and there were no crossings among these MOs. For all three molecules the best agreement between calculated and experimental IPs involved the conformers with the O–C=O

plane making an angle of  $60^\circ$  with the pseudo-three-fold axis [through C(1)–C(4)] of the bicyclo-octane moiety (9). These HAM/3 IPs are listed in the Table.

#### DISCUSSION

It is useful to compare the low IPs of the five molecules considered here with those of related molecules measured by other workers. The IP correlation diagram shown in Figure 2 also includes data for bicyclo[2.2.2]oct-2-ene (10),<sup>7</sup> and 2-azabicyclo[2.2.2]oct-5-ene (11).<sup>6</sup>



An obvious feature of the correlation diagram is that the molecule of particular interest (3) contains two strongly electron-withdrawing groups. The ketone carbonyl group in (6) stabilizes the  $\pi_{CC}$  MO of (10) by 0.84 eV, and the urethane carbonyl group in (7) stabilizes the  $\pi_{CC}$  of (10) by 0.42 eV, a difference of 0.42 eV. The ethylene bond in each of (6) and (7) has little effect on their first IPs, which are attributed to the  $n_O$  and  $n_N$  localized orbitals respectively, as indicated by comparison with the first IPs of the respective octanes (4) and (5).

The higher electronegativity of ketone carbonyl compared to urethane carbonyl is shown by the shifts in higher IPs of the bicyclo-octane moiety. In particular, between 9 and 14 eV, bicyclo[2.2.2]octane shows

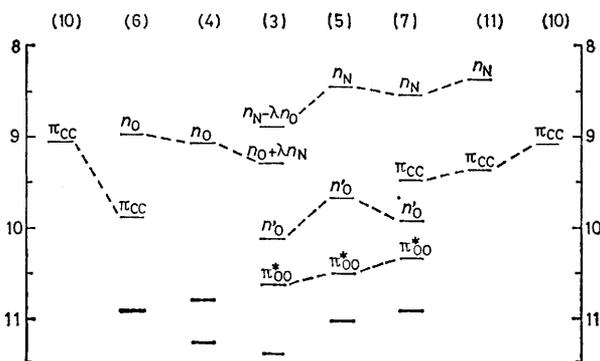


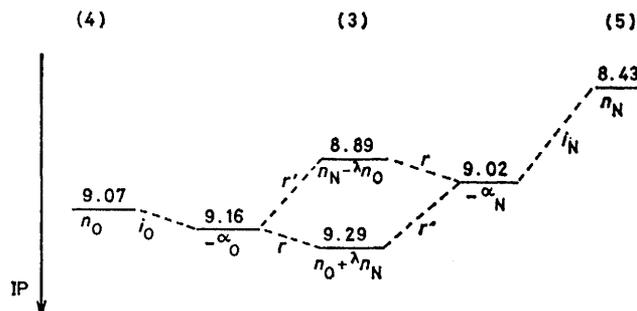
FIGURE 2 IP correlation diagram comparing (3)–(7) with the related molecules (10) and (11)

two groups of overlapped bands centred at 10.0 and 12.8 eV, respectively.<sup>7</sup> In (4) these have moved to 11.2 and 13.6 eV, respectively, showing a mean stabilization of 1.0 eV, whereas in (5) the corresponding band centres of 10.6 and 13.2 eV represent a mean shift of 0.5 eV. The mean IP shifts for ketone carbonyl and urethane carbonyl hence favour the ketone carbonyl group by 0.5 eV.

For (3) the higher bicyclo-octane IPs are centred at 11.7 and 13.9 eV, showing a mean shift of 1.4 eV from the bicyclo[2.2.2]octane values. In these terms the inductive effect of stabilization is hence nearly additive for the two substituents in (3).

However the inductive effect of each substituent on the other is not as great, since the first and second IPs of (3) represent increases of 0.46 and 0.22 eV over the first IPs of (5) and (4), respectively. The HAM/3 calculation indicates that there is a through-space interaction of the carbonyl oxygen lone-pair  $n_O$  and the nitrogen lone-pair  $n_N$  in compound (3). A simple Hückel pattern based on the measured IPs gives a semi-quantitative description of this interaction which is in good agreement with the HAM/3 data (Scheme).

The inductive effects of each substituent group leave the two lone-pairs very close in energy (a difference of 0.14 eV). The solution of the Hückel matrix produces a resonance interaction integral  $\beta_{NO}$  of  $-0.19$  eV and delocalized molecular orbitals separated by 0.40 eV.



SCHEME Hückel pattern for compounds (4), (3), and (5)

These are derived as  $\phi_1 = 0.82n_N - 0.57n_O$  and  $\phi_2 = 0.82n_O + 0.57n_N$ , showing mixing coefficients similar to the normalized values taken from the HAM/3 calculation, namely  $\phi_1 = 0.89n_N - 0.45n_O$  and  $\phi_2 = 0.86n_O + 0.52n_N$ .

The HAM/3 calculation indicates that there is virtually no hydrocarbon through-bond contribution in this interaction.

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