

Ultraviolet photoelectron spectra of fenchone, camphor and bromocamphor

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Abstract

He(I) photoelectron spectra are reported for the methyl-substituted monoketones fenchone, camphor and bromocamphor. We discuss the observed n(O)-binding energy shift in terms of substituents' effects on the electron density in the carbonyl bond. © 1997 Elsevier Science B.V.

Keywords: Carbonyl; He(I); Methyl group; Monoketone; Ultraviolet photoelectron spectroscopy

1. Introduction

Ultraviolet photoelectron spectroscopy (UPS) provides information about the electronic structure of molecules. Much work has been invested in UPS of carbonyl compounds in order to determine the influence of various substituents on the carbonyl C=O bonding [1–3]. Changes in intramolecular electronic interactions are concluded by analyzing the electron binding energy (BE) of the oxygen non-bonding orbital ($E_{n(O)}$).

A large number of bicyclic mono- and diketones have been investigated. Bischof et al. [4] have measured $E_{n(O)}$ in the unsubstituted bicyclic monoketone 2-norbornanone (Fig. 1(a)). Characteristic shifts in $E_{n(O)}$ arising from methylation have been reported for representative derivatives of 2-norbornanone [5–8]. Investigations of dike-

tones have been focused on the determination of the $n_+(O)-n_-(O)$ splitting of the n(O) peak [7,8]. The results were interpreted on the basis of direct ('through-bond') and indirect ('through-space') interactions of the two carbonyl groups [9–11].

In this report we present the He(I) photoelectron spectra of the bicyclic monoketones fenchone (1a), camphor (1b) and bromocamphor (1c). References are 2-norbornanone (2a), 6,6-dimethyl-2-norbornanone (2b) and 3,3-dimethyl-2-norbor-

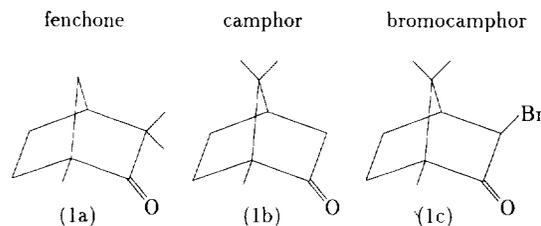


Fig. 1. Structural formulas of the bicyclic monoketones (1a, 1b, 1c) measured in this study.

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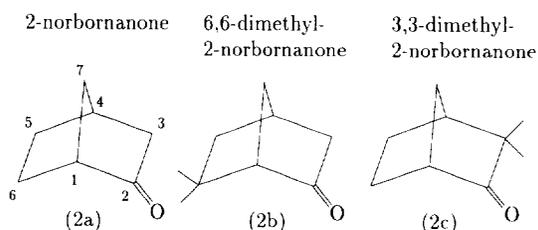


Fig. 2. Structural formulas of the bicyclic monoketones (2a, 2b, 2c) measured by Frost et al. [7].

nanone (2c) measured by Frost et al. [7]. The molecular structure of these molecules is presented in Figs. 1 and 2. It is the goal of this investigation to determine the influence of different arrangements of methyl groups in the isomers fenchone and camphor, and the substitution of a H atom in camphor by the more electronegative Br atom in bromocamphor on the electron density in the C=O group indicated by $E_{n(O)}$.

2. Experimental

Commercial (1*R*)-(–)-fenchone (1,3,3-trimethyl-2-norbornanone), (1*R*)-(+)-camphor (1,7,7-trimethyl-2-norbornanone) and [(1*R*)-endo]-(+)-3-bromocamphor (*x*-bromo-*d*-camphor) (Aldrich Chemie and Co KG) had been filled in glass flasks connected by a valve to the measurement chamber. A cubic gas cell with 3 cm sidelength was designed for these experiments to increase the sample pressure relative to the permitted total pressure (10^{-3} Pa) in the measurement chamber. There were three pin-holes in the walls of the cell (3, 5 and 4 mm in diameter): for the exciting He(I) radiation, the photoelectrons and a pipe connecting the gas cell and the gas inlet valve. Solid bromocamphor (powder) was heated at 60°C to increase the vapour pressure. Fenchone and camphor were available as liquids.

The He(I) photoelectron spectra were obtained using an electron energy analyzer CLAM 2 (Fisons Instruments) working in the constant energy mode (10 eV) and a VUV-discharge lamp HIS 13 [12] providing a He(I) photon flux of $4 \times 10^{12} \text{ s}^{-1}$.

The energy calibration was performed by measuring the peak positions of Ar $3p_{3/2}$ (BE = 15.759 eV), Kr $4p_{3/2}$ (BE = 14.0 eV) and $N_2 3\sigma_g^+$ (BE = 15.58 eV) [13] before and after scanning the sample spectra. The experimental uncertainty of the given BE was less than 0.05 eV, checked by repeating the measurements. The energy resolution was 0.1 eV (Ar $3p_{3/2}$ full width at half maximum (FWHM)). Spectra were accumulated over 20 scans with step widths of 0.05 eV and an integration time of 0.25 s per step.

3. Results and discussion

The He(I) photoelectron spectra of fenchone, camphor and bromocamphor are shown in Fig. 3. All spectra exhibit the first ionization potential near 9 eV, which is assigned to $E_{n(O)}$ corresponding to the oxygen non-bonding orbital clearly separated from the energy region containing strongly overlapping bands beginning at about 10 eV [5–7]. The fenchone spectrum is in good agreement with that reported previously by Frost et al. [7].

Comparing the spectrum of camphor (1b) with fenchone (1a) we observe a decrease in $E_{n(O)}$ from 8.94 (1b) to 8.86 eV (1a) obtained by a least-squares fitting routine assuming Voigt profiles. This shift (-0.12 eV) can be explained by the electron donor effect of the methyl substituents (I^- -effect), which increases the more the Cou-

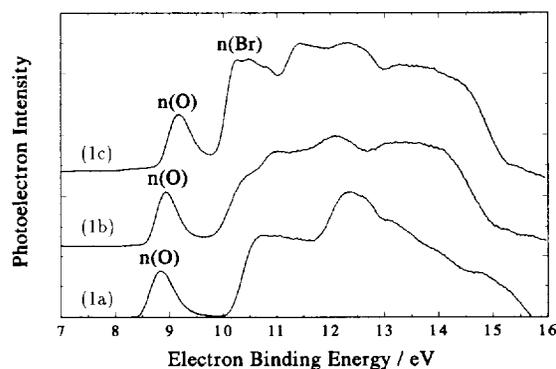


Fig. 3. He(I) photoelectron spectra of fenchone (1a), camphor (1b) and bromocamphor (1c).

lomb repulsion potential felt by the n(O) electrons the shorter the distance between the methyl substituents and O is. This result is confirmed by an corresponding $E_{n(O)}$ shift (-0.11 eV) reported by Frost et al. [7] for 2b and 2c.

Frost et al. [7] observed a decrease in $E_{n(O)}$ with an increasing number of methyl groups in bicyclic monoketones. It must be emphasized that the $E_{n(O)}$ of camphor (8.94 eV), containing three methyl groups, lies between the values of both the dimethyl-substituted compounds 2b (9.0 eV) and 2c (8.89 eV) [7]. This result suggests that the position and number of methyl groups at bicyclic monoketones change the electron density in the carbonyl group in a similar way.

To generalize the results, we suggest an $E_{n(O)}$ dependence on number and distance in the order for progressive negative shifts: 9.17 eV (2a) \rightarrow 9.0 eV (2b) \rightarrow 8.94 eV (1b) \rightarrow 8.89 eV (2c) \rightarrow 8.86 eV (1a).

In general, larger n(O) FWHM can be attributed to a loss of the non-bonding character, giving rise to a formation of vibrational fine structure [14]. We observe a systematic increase of n(O) FWHM, including the values of Frost et al. [7], in the sequence: 2a (0.36 eV), 2b (0.37 eV) (non-neighbouring methyl group) \rightarrow 1b (0.45 eV) (one neighb.) \rightarrow 2c (0.49 eV) (two neighb.) \rightarrow 1a (0.50 eV) (three neighb.), which evidences the electronic interaction of the n(O) lone pair with the methyl groups as the origin of n(O)-peak broadening.

Comparing the spectra of bromocamphor (1c) with camphor (1b), all peaks shift to higher BE. For the n(O) peak, we observe a BE shift from 8.94 (1b) to 9.18 eV (1c) as a result of the high electronegativity of bromine, with the expected influence on the valence electron density in the C=O bonding region (I^- -effect). Two pronounced new features (BE = 10.25, 10.5 eV) in the bromocamphor spectrum are explained as Br lone pairs (n(Br)) as can be derived from related data for $E_{n(Br)}$ (≈ 11 eV) [14].

4. Conclusion

The n(O) electron binding energies obtained by UPS have been used to characterize the influence of different numbers and distances of methyl groups in fenchone and camphor, and of the substitution of a H atom by a Br atom in bromocamphor on the valence electron density in the C=O region. We observed a decrease of $E_{n(O)}$ with decreasing distances between the C=O and methyl groups. A substituted Br atom causes increasing $E_{n(O)}$. These results agree with the expectation of an I^+ -effect of methyl groups and an I^- -effect of bromine. Increasing FWHM are found to correlate with the number of nearest methyl groups, giving rise to electronic interaction between O-lone pair and methyl-like orbitals.

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