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# The Thermal Isomerisation Benzoazetine - 6-Methylene-2,4-cyclohexadien-1-imine: a Photoelectron Investigation

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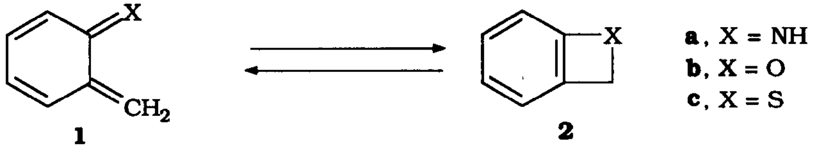
***Abstract:*** *The flash vacuum thermolyses of 1,2,3,4-tetrahydroquinoline 3, o-aminobenzylalcohol 4 and o-aminobenzylamine 5 were performed at temperatures from 923 to 1273 K and monitored by photoelectron spectrometry. While thermolyses at 923-1073 K led to the until now undescribed benzoazetine 2a, 6-methylene-2,4-cyclohexadien-1-imine 1a was obtained at 1173-1273 K.*

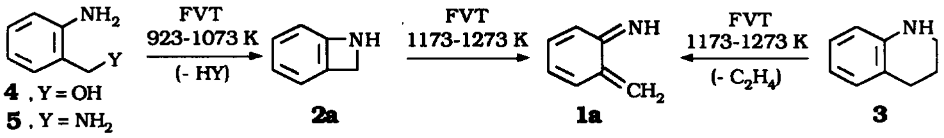
We reported recently the synthesis of 6-methylene-2,4-cyclohexadien-1-imine **1a** and of related o-quinonoids by flash vacuum thermolysis (FVT) of 1-hetero-1,2,3,4-tetrahydronaphthalenes[1]. Despite an EHT calculation[2] favoring the o-quinonoids **1a-c** against their bicyclic isomers **2**, benzothiete **2c** is experimentally known as the thermodynamically stable isomer in the equilibrium **1c** ↔ **2c**[3], while the oxygenated derivative **1b** is obviously more stable than its unknown isomer **2b** (see refs cited in [1]).



**1** **2**

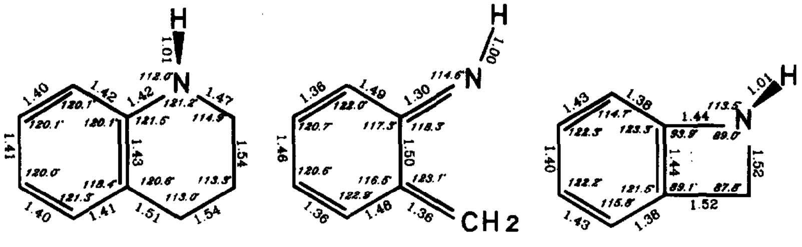
**a**, X = NH
**b**, X = O
**c**, X = S

Whereas the generation of **1a** by FVT of precursors **3-5** was clearly demonstrated[1], the investigation methods employed did not allow us to get precise informations about the relative stability of isomers **1a** and undescribed benzoazetine **2a** (7-azabicyclo[4.2.0]octa-1,3,5-triene) and their possible interconversion, owing to either the rapid polymerisation of **1a** upon warming up in the condensed phase during IR/UV analysis or to the similarities expected between the mass spectra of **1a** and **2a**. On the other hand, the coupling of FVT and photoelectron spectrometry (PES) proved to be most efficient for the gas phase investigation of such tautomeric equilibria[4] and we report herein our observations and conclusions, concerning the PES analysis of the reactive species obtained by FVT of compounds **3-5**, and demonstrating the formation of benzoazetine **2a** at 923-1073 K (from **4** or **5**) as well as its thermal isomerisation into **1a** at 1173-1273 K.



**4**, Y = OH
**5**, Y = $NH_2$
**2a** **1a** **3**

The experimental spectra have been compared to MNDO theoretical results, the ionization potentials (IP's) being estimated for optimized geometries within Koopman's approximation. These geometries are reported hereafter for compounds **3**, **1a**[5], and **2a** (Fig. 1). Compound **2a** is found to be energetically favored over **1a** by 24.34 kJ.mol$^{-1}$. Similar calculations performed on **1b**-**2b** and **1c**-**2c** show, in agreement with the reported experimental results, an important stabilization for **2c** over **1c** (103.88 kJ.mol$^{-1}$), the o-quinonoid form **1b** being on the other hand more stable than **2b** by 36.89 kJ.mol$^{-1}$.



**3** ($E_F$ = 61.81 kJ.mol$^{-1}$) **1a** ($E_F$ = 253.74 kJ.mol$^{-1}$) [5] **2a** ($E_F$ = 229.40 kJ.mol$^{-1}$)

**Fig. 1. Optimized geometries and $E_F$ for compounds 3, 1a and 2a**

The FVT-PES experiments have been performed on a Helectros 0078 spectrometer under a $10^{-5}$ hPa pressure (see ref. [6] for experimental details). The PE spectrum 1 (Fig. 2) of precursor **3** shows three distinct bands at 7.5, 8.5 and 10.1 eV, with a shoulder at 11.1 eV, the first band corresponding to the ionization of the molecular orbital (MO) delocalized between the aromatic ring and nitrogen atom. The second one is associated with the ejection of electrons from the MO derived from the antisymmetric combination of the ring $\pi_{C=C}$ system. The last band and its shoulder arise from ionization of the nitrogen lone pairs $n_{N\pi}$ and $n_{N\sigma}$. The discrepancy between experimental IP values and calculated orbital energies (Fig. 3) is due to neglecting polarization effects, particularly for the MO's localized on nitrogen lone pairs.

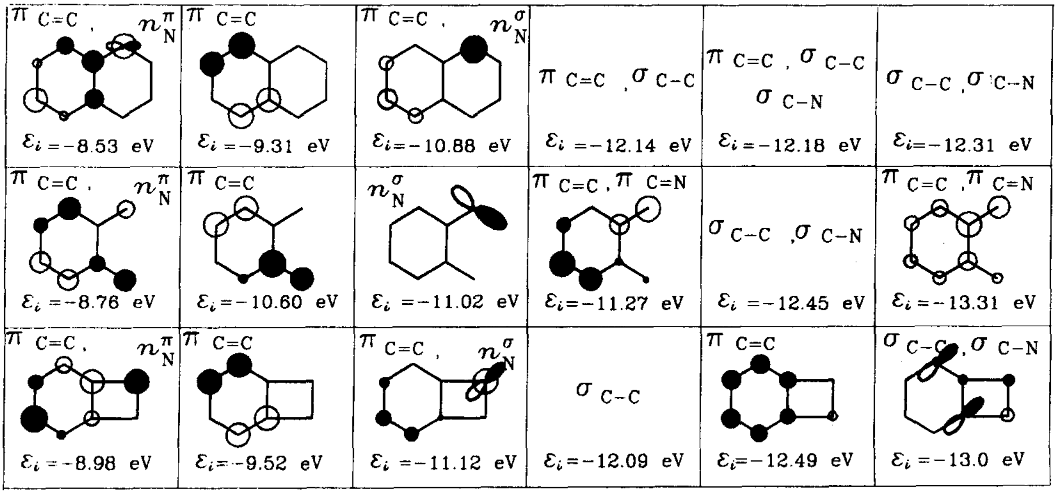


**Fig. 3. Calculated orbital energies for compounds 3, 1a and 2a**

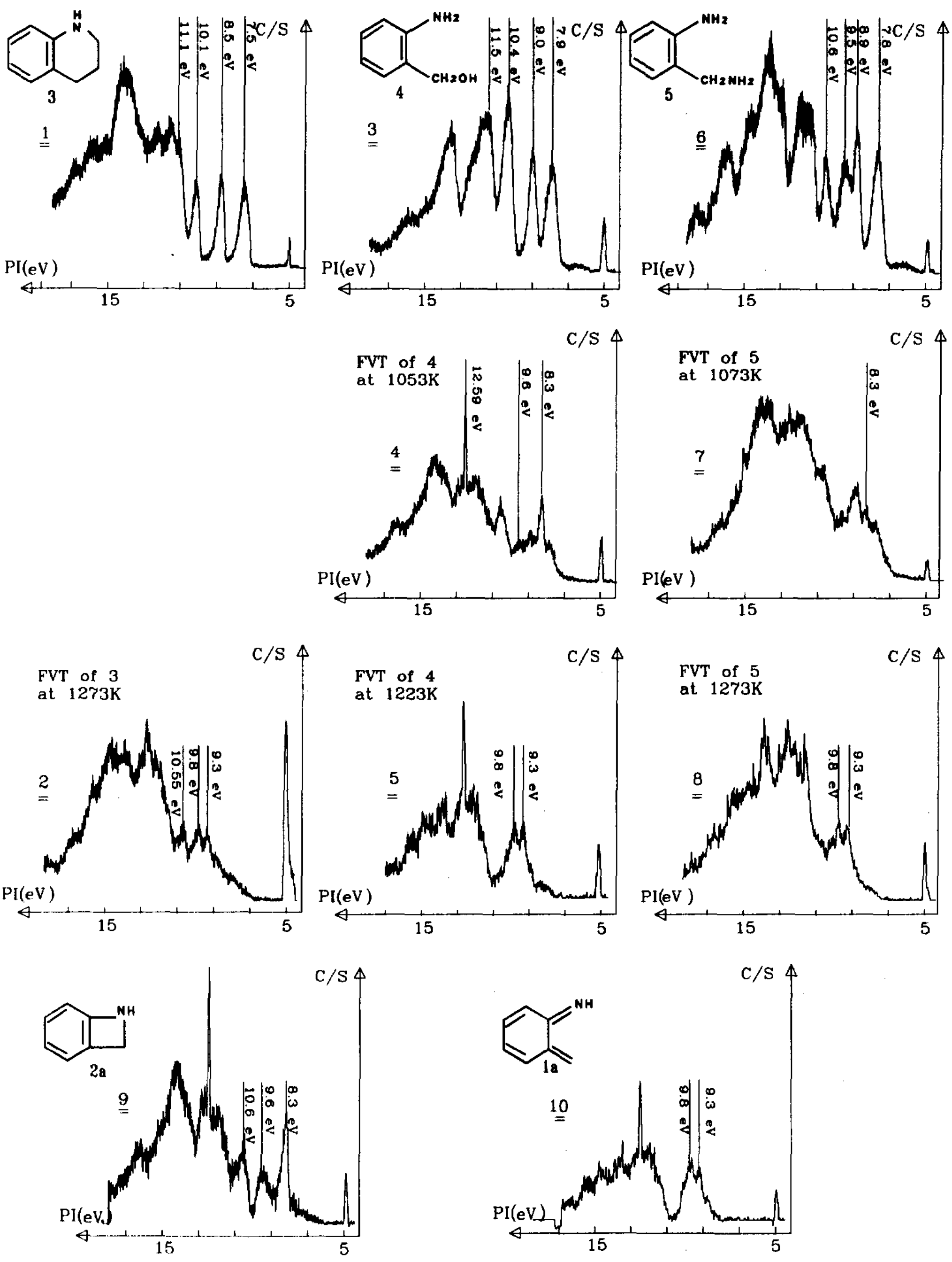


Fig. 2. Photoelectron spectra 1 - 10

The retro-Diels-Alder reaction of **3** begins at a FVT temperature of 1173 K. Three new bands are observed at 9.3, 9.8, and 10.55 eV ($C_2H_4$). Traces of starting material **3** remain observable at 1273 K (Fig. 2, spectrum 2). A comparison between these experimental values and the orbital energies calculated for **1a** and **2a** (Fig. 3) supports the attribution of the observed spectrum to the o-quinonoid species **1a**, when the polarization effect, estimated to be *ca.* 1 eV for the ionization of the lone pair $n_N\sigma$, is taken into account. The thermodynamically less stable form **1a** appearing thus to be that likely observed at 1273 K, we investigated also the FVT of compounds **4** and **5** (spectra 3 and 6) which takes place at lower temperatures[1].

Two distinct steps are observed in the FVT of o-aminobenzylalcohol **4**, beginning at 923 K. In the first one (1053 K, spectrum 4), water is eliminated and two new bands appear at 8.3 and 9.6 eV. The second step (1223 K, 5) corresponds to the disappearance of the bands at 8.3 and 9.6 eV and their replacement by bands at 9.3 and 9.8 eV, already observed (2) in the FVT of tetrahydroquinolin **3**. The difference spectrum 9, resulting from the subtraction of the spectrum of **4** (3) from that obtained at 1053 K (4), shows clearly the bands at 8.3 and 9.6 eV attributed to the bicyclic isomer **2a**. The first band at 8.3 eV corresponds to the ionization of the electron of the MO combination of $\pi_{C=C}$ and $n_N\pi$ orbitals. The second one at 9.6 eV is associated with the $\pi_{C=C}$ orbitals of the aromatic ring. The ionization of the $n_N\sigma$ and third $\pi$ orbitals is responsible for the band at 10.6 eV. The spectrum 10, corresponding to **1a**, is obtained by subtracting the spectrum of **4** (3) from that recorded in the FVT of **4** at 1223 K (5).

A similar result is obtained in the FVT of o-aminobenzylamine **5**. Elimination of ammonia begins at 923 K and the spectrum obtained at 1073 K (7) shows again the first band at 8.3 eV attributed to **2a**. The band at 9.6 eV is obscured by that of remaining **5**. When the FVT temperature is raised to 1273 K, the spectrum 8 obtained presents the expected bands of **1a** at 9.3 and 9.8 eV.

The formation of the thermodynamically more stable isomer **2a** in the FVT of **4** or **5** at 923-1073 K confirms unambiguously that the o-quinonoid isomer **1a** is the one observed in the higher temperature FVT of precursors **3**, **4** and **5**. Thus, the 1,4-elimination, invoked for o-substituted phenols or related precursors and leading to o-quinonoids **1**[7], appears in fact, at least in the case of **4** and **5**, to be a four-centered elimination giving benzoazetine **2a**, followed at upper temperature by electrocyclic opening to **1a**.

## References and notes

1. Letulle, M.; Guenot, P.; Ripoll, J.L. *Tetrahedron Lett.* **1991**, *32*, 2013-2016.
2. Kolshorn, H.; Meier, H. Z. *Naturforsch.* **1977**, *32a*, 780-782.
3. Kanakarajan, K.; Meier, H. *J. Org. Chem.* **1983**, *48*, 881-883. Meier, H.; Eckes, H.L.; Niedermann, H.P.; Kolshorn, H. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1046-1048. Schmidt, M.; Meier, H.; Niedermann, H.P.; Mengel, R. *Chem. Ber.* **1990**, *123*, 1143-1148. Schweig, A.; Diehl, F.; Kesper, K.; Meyer, H. *J. Mol. Struct.* **1989**, *198*, 307-325.
4. Schweig, A.; Vermeer, H.; Weidner, U. *Chem. Phys. Lett.* **1974**, *26*, 229-233.
5. The (E)-**1a** is more stable by 5.95 $kJ.mol^{-1}$ than the (Z) isomer.
6. Vallée, Yo.; Ripoll, J.L.; Lacombe, S.; Pfister-Guillouzo, G. *J. Chem. Research (S)* **1990**, 40-41, *(M)* **1990**, 0401-0412.
7. Wagner, H.U.; Gompper, R. Quinone Methides. In *The Chemistry of the Quinonoid Compounds (part 2);* Patai, S. Ed.; John Wiley and Sons, Inc.: New York, 1974; pp. 1145-1178. Boekelheide, V. *Acc. Chem. Res.* **1980**, *13*, 65-70.

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