AN INVESTIGATION OF TERPENE HYDROCARBONS OF THE CARANE SERIES BY PHOTOELECTRON SPECTROSCOPY

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2- and 3-Carenes and carane have been studied by PE spectroscopy. On the basis of an analysis of orbital interactions and information obtained from the PE spectra of model compounds an assignment has been made of the bands corresponding to ionization from the molecular orbitals of the double bond and of the cyclopropane ring.

The chemical transformations of terpenoids of the carane series are largely due to the presence of a cyclopropane ring (CPR) in the molecule of each of these compounds. In its turn, the reactivity of this structural fragment determines the nature and energetics of its highest occupied molecular orbitals (HOMOs). One of the most informative modern methods of studying the electronic structures of reactive fragments of molecules is photoelectron (PE) spectroscopy. In the present paper we give the results of a study of the PE-spectroscopic method of the natural terpenes 3- and 2-carenes and the product of their hydrogenation, carane.

In the PE spectra of all three of the compounds that we investigated (Fig. 1) there are well-resolved bands in the region of low ionization energies (8–10 eV) corresponding to ionization from the π-MO of the CPR and the double bond. In the region of higher energies the spectrum has a complex, weakly resolved, structure, which is due to ionization from σ-MOs lying close to one another (with respect to energy). We have therefore limited ourselves to a consideration of the first two or three ionization potentials (IPs). They present the greatest interest, since they correspond to ionization from the MOs responsible for the reactivity of these compounds. The values of the vertical IPs of the compounds investigated and model compounds are given in a correlation diagram (Fig. 4).

It is known that the HOMOs of cyclopropane are doubly degenerate, one of these orbitals being symmetrical and the other antisymmetrical with respect to the plane of symmetry [1]. In the PE spectrum of cyclopropane there are two bands, 10.53 and 11.30 eV, which is due to a manifestation of the Jahn–Teller effect [2]. Thus, according to Koopmans' theorem [3] the energy of the HOMO of cyclopropane amounts to −10.9 eV [4]. The introduction of alkyl substituents leads to the removal of the degeneracy [5]. Thus, in the carene molecule the CPR is bound to four alkyl groups: two geminal methyl groups and two cyclic methylene groups. To analyze the first two IPs of carane, which correspond to ionization from the π-MOs of the CPR, it is sufficient to limit ourselves to a consideration of this fragment of the molecule. Here we shall use the effective parameters obtained from the PE spectra of compounds close in structure to that under investigation. As the model compounds we selected 1,1-dimethylcyclopropane and norcarane.

The fragment of the carane molecule under consideration possesses C_s symmetry; the methyl groups of the six-membered ring exert a destabilizing action on the two orbitals of the CPR, while the methyl group perturbs only the antisymmetric orbital. Consequently, one of the IPs of carane should be close to the IP_1 of norcarane (9.46 eV [5]). In actual fact, IP_2 for carane is 9.51 eV; this obviously corresponds to ionization from the carane orbital with a' symmetry. This orbital (Fig. 2, A) is an antibonding combination of the e_s orbital of cyclopropane and the $\left(\pi_{CH_2}+\pi'_{CH_2}\right)$ MO of the methylene groups. The inductive effect of the methylene groups also leads to the destabilization of the e_s orbital of the CPR and, thus, the total change in the orbital energy amounts to 1.4 eV.

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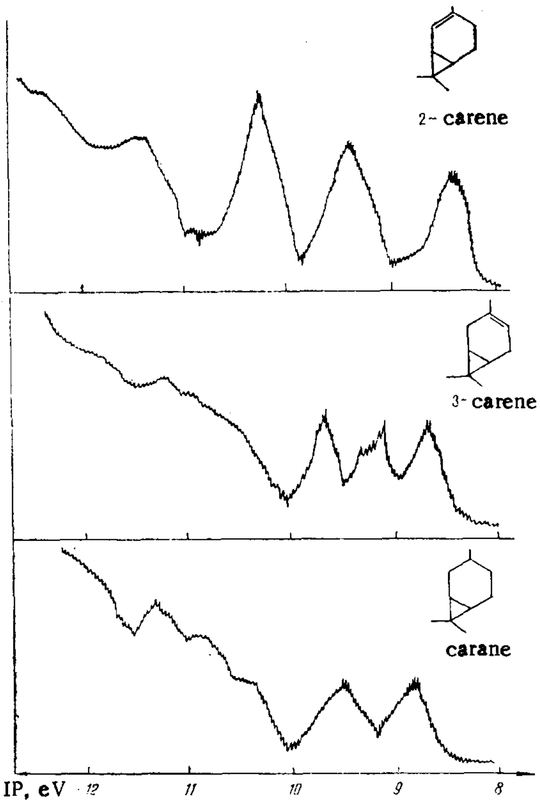

Fig. 1. Photoelectron spectra of hydrocarbons of the carene series.

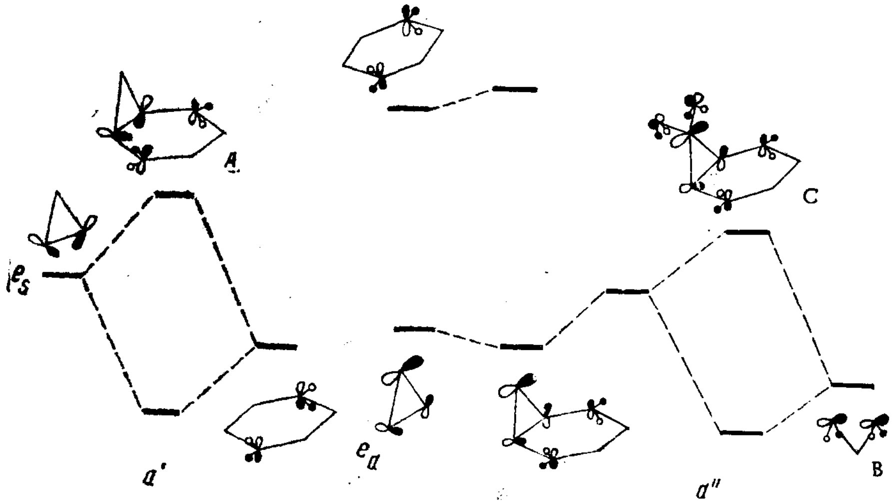

Fig. 2. Interaction of the orbitals of the structural fragments of the carene molecules.

The e_a antisymmetrical orbital of CPR can be combined with MOs of the methyl and methylene fragments, ensuring the maximum overlap. For the methyl groups, this is the $(\pi_{CH_3}+\pi'_{CH_3})_{CH_3}$ combination [6] (Fig. 2B). There are no methylene orbitals of suitable symmetry; their antibonding component may, in its turn, be combined with MOs of the *a*'' type (Fig. 2, e_a), but because of the great difference in the energies of the initial MOs the effect of this interaction is insignificant and, therefore, the influence of the methylene groups is almost purely inductive. It can be seen from the PE spectra of norcarane [5] that the total effect amounts to 0.9 eV (10.91 – 10.01 eV). The influence of the gem-dimethyl grouping, which is also due to the effects of induction and conjugation, amounts to 1.1 eV, which follows from a comparison of the IPs of cyclopropane and of 1,1-dimethylcyclopropane [6] (10.91 – 9.80 eV).

Since other interactions capable of causing an appreciable change in the energy of this MO (Fig. 2C) are absent, the total lowering of the IP for this orbital should amount to ~2 eV. The band at 8.84 eV observed in the spectrum of carane agrees fairly well with the calculated value (10.9-2.0 eV) and corresponds to ionization from the carane MO of symmetry a''.

Thus, on the basis of PE spectrum it is possible to arrive at the conclusion that the bonds of the CPR in the carane molecule are comparatively strong. The HOMO of carane is antisymmetric, and since it is precisely this orbital that makes the main contribution to bonding between the C_1—C_7 and C_6—C_7 atoms (Fig. 2C), it may be concluded that these bonds will be less strong than the C_1—C_6 bond. This point of view is in harmony with results obtained by the semiempirical MINDO/3 method, on the basis of which a methyl substituent is considered as a formal π-acceptor [7], causing, like the cyano group a change in the geometry of the CPR. Analysis of the figures given in [7] shows that the simultaneous presence of two alkyl substituents in position 1 of cyclopropane and of two alkyl substituents in positions 2 and 3 should cause a lengthening of the C_1—C_2 and C_1—C_3 bonds to a greater degree than the lengthening of the C_2—C_3 bond (in the carane molecule, these correspond to the C_1—C_7 and C_6—C_7 bonds and the C_1—C_6 bond).

For the norcarane molecule, the situation is the opposite (Fig. 4): the C_1—C_6 bond will be less strong, since the main contribution to bonding between these atoms is made by the MO with the greater energy. However, both in the case of norcarane and in the case of carane the difference in the energies of the two highest MOs is small (0.55 and 0.67 eV, respectively).

The 3-carene molecule differs from the carane molecule by the presence of a double bond. The influence of the vinyl methyl group can be reduced to its interaction with the double bond [8] and the 3-carene molecule be considered as belonging to the C_s symmetry group.

The vertical IP_1 of 1-methylcyclohexene amounts to 8.67 eV [9]. On comparing this value with IP_1 of 3-carene (8.61 eV) it can be seen that the latter corresponds to the removal of an electron from a practically unperturbed π-MO of the double bond of the methylcyclohexene ring. The small increase in the energy of the MO is due to the positive inductive effect of the CPR.

Correspondingly, the energy of the MO with the a' symmetry of the molecular fragment with the three-membered ring should fall in comparison with the IP_2 of carane (9.51 eV). Thus, the IP_3 of 3-carene, which is 9.66 eV, corresponds to ionization from a 3-carene MO of a' symmetry.

The IP_2 of 3-carene (9.16 eV), consequently, corresponds to ionization from a MO of a'' symmetry. The rise in the IP_2 of 3-carene as compared with the IP_1 of carane (8.84 eV) is due primarily to the negative inductive effect of the double bond, but the ΔIP value of 0.32 eV shows that there is also a positive orbital interaction with a higher MO. There are no filled orbitals with this symmetry and, consequently, a second-order perturbation takes place due to interaction with the antibonding MO of the double bond (Fig. 3). However, because of the large difference in the energy of the interacting MOs the perturbation will be small, and so will that due to induction, and the total effect amounts to 0.32 eV.

This assignment of the bands in the PE spectrum of 3-carene can be compared with its reactivity, especially in electrophilic addition reactions. Thus, in the hydrochlorination of 3-carene the first molecule of hydrogen chloride adds to the CPR and the second to the double bond [10]. In the oxymercuration reaction, conversely, the double bond undergoes attack more readily [1]. In view of the energy of the corresponding MOs obtained from the PE spectra, this difference in the direction of the attack of the electrophil can be explained in the following way: the proton – a hard acid – attacks a harder base preferentially, which in this molecule is the cyclopropane fragment (IP = 9.16 eV); the soft acid $[HgOAc]^+$ attacks the softer base – the double bond (IP = 8.61 eV). It must be mentioned that both in this case and in the case of carane the difference in the energies of these two MOs is small, and the question is only that of the regioselectivity, and not of the regiospecificity, of these reactions, as is observed in experiment [11].

The PE spectrum of 2-carene is more complicated to interpret because the position of the double bond completely deprives the molecule of symmetry and thereby creates the necessity for considering only pairwise interactions of the individual fragments.

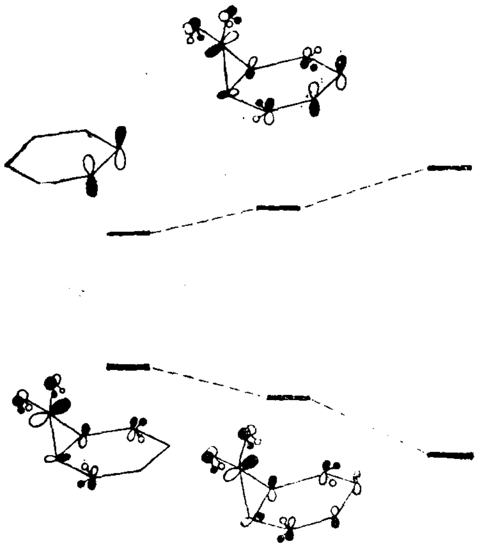

Fig. 3. Interaction of the orbitals of a'' symmetry of the structural fragments of the 3-carene molecule.

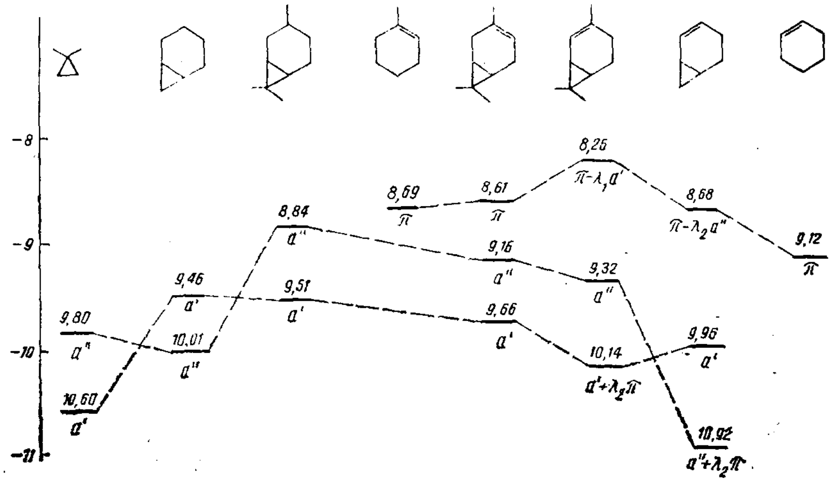

Fig. 4. Correlation diagram of the energy levels of the MOs of the compounds investigated and of model compounds.

The IP1 of 2-carene, which is 8.26 eV, corresponds to ionization from the HOMO of the double bond of the 1-methylcyclohexene ring perturbed by the presence of the CPR. This perturbation is due both to orbital and to inductive interactions. The magnitude of this perturbation (8.69 − 8.26 = 0.43 eV) shows that the orbital interaction of the CPR and the double bond is slight: for the cyclopropane/double bond system in the s-trans conformation system when conjugation and, consequently, perturbation are at maximum levels, the magnitude of this perturbation amounts to 1.6 eV [12].

It can be seen from Fig. 2 that when a gem-dimethyl grouping attached to the CPR is present, appreciable overlapping is achieved in the interaction of the π-MO of the double bond with the CPR orbital having the a'symmetry. By using figures obtained from the PE spectra of 2-carene, carane, and 2-norcarene it is possible to separate the contributions of the conjugation effect and of inductive interaction. In the 2-norcarene molecule, which does not contain a gem-dimethyl grouping, the π-MO of the double bond interacts with the e_a orbital of the CPR and exerts only an inductive action on the e_s orbital [5]. It can be seen from a comparison of the corresponding IP values for norcarane and 2-norcarene that it amounts to 0.5 eV (9.46 and 9.96 eV, respectively [5]). By using this value for the case of 2-carene, it can be seen that the orbital interaction lowers the energy of the MO with the a' symmetry of 2-carene by 0.10-0.15 eV ($IP_{a'}$ for carane = 9.51 eV; 9.51 + 0.5 = 10.01 eV; IP_3 for 2-carene = 10.14 eV).

The IP_2 of 2-carene therefore corresponds to ionization from a carane orbital of the a'' type. The higher value of the IP_2 and 2-carene (9.32 eV) in comparison with IP_1 of carane is also due to the inductive influence of the substituents. ΔIP amounts to ~0.5 eV, which is close to the corresponding parameter for the a' MO.

The change in the energy of the MOs of the double bonds and the CPR enables the angle between the axes of the p-orbitals of these fragments to be calculated by using an expression for second-order perturbation [5]. The basis energies are determined in the following way: the energy of the MO with the a' symmetry of the fragment containing the CPR is 9.51 + 0.5 = 10.01 eV (the inductive influence of the double bond has been taken into account); the energy of the π-MO of the double bond is 8.69 − 0.2 = 8.49 eV (the inductive influence of the CPR has been taken into account [4]). The coefficients of the wave function of the p-orbitals in the MOs of the double bond and in the e_S MO of cyclopropane are equal to one another and amount to $1/\sqrt{2}$. Thus, according to [5], we obtain the expression

$$\left(\frac{10.14-8.26}{2}\right)^2-\left(\frac{10.01-8.49}{2}\right)^2=\left(\beta\cdot\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\cdot\cos\theta\right)^2.$$

Taking the resonance integral for the Walsh interaction of the MOs and the double bond as −1.9 eV [4], we obtain $\cos\Theta=0.587$, $\Theta=54°$.

Of course, the value obtained is somewhat approximate, but it agrees well with the value measured on a molecular model for the pseudochair conformation (50-55°). For the pseudoboat conformation the corresponding angle is 5-10°. Thus, the results obtained show the preferential nature of the pseudochair conformation for the 2-carene molecule, as has also been shown by other methods [13].

EXPERIMENTAL

The He-1 photoelectronic spectra of the compounds investigated were obtained on a ES 3201 spectrometer with a resolution of 40 meV. The spectra were calibrated from the xenon 12.13 and 13.43 eV lines.

The hydrocarbons investigated were purified by preparative GLC on a PAKhV-06 chromatograph using a 8000 × 4 mm packed column with a N-AW-DMCS solid support (grain size 0.250-0.316 mm) and diethyleneglycol adipate as the stationary phase (20% of the weight of the support); temperature 90°C; rate of flow of carrier gas (helium) 80 ml/min.

The 3-carene was isolated from pine oleoresin turpentine; purity 100%, d_4^{20} 0.8638, n_D^{20} 1.4730, $[\alpha]_D^{20}+16.3°$.

The 2-carene was obtained by the isomerization of 3-carene with N-lithioethylenediamine [14]. Purity 99.5%, d_4^{20} 0.8623, n_D^{20}1.4738, $[\alpha]_D^{20}+78.2°$.

The carane was obtained by the hydrogenation of 3-carene on platinum black in absolute ethanol. Purity 99.9%, d_4^{20} 0.8398, n_D^{20} 1.4568, $[\alpha]_D^{20}-4.3°$.

SUMMARY

3- and 2-Carenes and carane have been investigated by PE spectroscopy. A correlation has been established between the ionization potentials of the individual structural fragments of the 3-carene molecule and its reactivity. It has been shown that the preferred conformation of the 2-carene molecule is the pseudo-chair conformation.

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^{13}C NMR SPECTRA OF A NUMBER OF PENTA- AND HEXACYCLIC TRITERPENOIDS DERIVED FROM GLYCYRRHETIC ACID

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The ^{13}C NMR spectra of 22 derivatives of 18α- and 18β-glycyrrhetic acids that have been investigated and an assignment of the signals has been made. It has been shown that a modification of the carboxy group of glycyrrhetic acid leads mainly to a change in the chemical shifts of the α-, β-, and γ-carbon atoms of ring E. The assignment of a number of signals has been confirmed by the use of the shift reagent Eu(fod)$_3$. It has been established that the C_{28} and C_{16} signals are the most sensitive to a change in the C_{18} configuration in the spectra of glycyrrhetic acid derivatives.

The high and varied biological activity of glycyrrhetic acid and its derivatives is arousing the interest of chemists in synthetic transformations of this acid connected with the modification both of the functional groups and of the carbon skeleton itself.

The most informative method of studying the structure of polycyclic compounds is ^{13}C NMR spectroscopy [1]. There are only two publications, by Ricca et al. [2, 3], on the ^{13}C NMR spectra of glycyrrhetic acid derivatives. These authors investigated and interpreted the ^{13}C NMR spectra of a number of derivatives of 18α- and 18β-glycyrrhetic acids and their 11-deoxo analogs, made an assignment of the signals, and showed that the configuration of the isomers at C_{18} can be determined from the chemical shifts (CSs) of a number of characteristic carbon atoms (C_{12}, C_{13}, C_{18}, C_{28}), the positions of the signals of which depend on the type of linkage of the D/E rings.

Using various methods, we have synthesized a number of derivatives of 18α- and 18β-glycyrrhetic acids (I-XXII) and have studied their ^{13}C NMR spectra.

Table 1 gives the values of the CSs and the multiplicities of the signals obtained from spectra with off-resonance proton suppression for the 18α- and 18β-glycyrrhetic acid derivatives investigated.

The spectra of compounds (I-IV and XVI-XVIII) practically coincided with those given in the literature [2, 3]. We are the first to have recorded and interpreted the ^{13}C NMR spectra of the other compounds.

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