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Frontier electronic structure in gas-phase epoxy and hydroxy cyclohexenes by means of photoelectron and electron transmission spectroscopies

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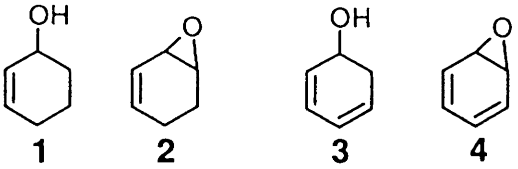
Ionisation energy (E_i) and electron affinity (E_a) values in benzene oxide, benzene hydrate, the corresponding monoenes and other related molecules have been measured by means of UV photoelectron spectroscopy and electron transmission spectroscopy. The valence filled levels do not show evidence for strong σ_{co}–π or oxygen lone pair–π mixing in the alcohols nor in the epoxides. Although the energy perturbations, caused by the hydroxy and epoxy substituents, to adjacent filled π orbitals are small, the electron transmission spectra show that the empty π^* orbitals are affected to very different extents, the epoxy substituent producing a sizeable electron affinity increase. This finding indicates the occurrence of strong interaction between the empty π^* orbitals and low-energy empty σ^* orbitals localised at the three-membered cycle. The experimental data have been compared with the orbital energies predicted by *ab initio* 3-21G calculations.

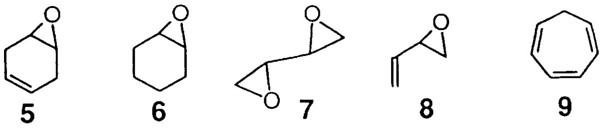
In a recent paper,[1] the rate constants for acid-catalysed carbon–oxygen bond breaking in alcohols and epoxides were compared. Normally, the rate constant values for this reaction are 10^6–10^7 times higher in epoxides than in the corresponding alcohols, as for instance in compounds **1** and **2** (Scheme 1). The authors found, surprisingly, that when the reactants are water and oxygen adducts of aromatic molecular systems, the kinetic rate constant ratios are much lower. In particular, for the benzene derivatives **3** and **4** this ratio is reversed, the epoxide being six times less reactive than benzene hydrate. These results were interpreted in terms of the normal reactivity of the hydrates and unusual unreactivity of the aromatic-derived oxides, even though carbon–oxygen bond breaking should be rate-determining in both cases. Among other possible factors, the authors tentatively explained the peculiar behaviour of arene oxides in terms of homoaromaticity. They evaluated that the 10^7-fold rate reduction for benzene oxide should imply a resonance stabilisation energy of at least 10 kcal mol^{-1}. Recent experimental measurements,[2] supported by calculations,[3] suggested a resonance energy of 5–8 kcal mol^{-1} in norcaradiene, the benzene oxide analogue where the oxygen atom is replaced by a CH_2 group. In benzene oxide, in addition to σ–π mixing, O lone pair–π interaction can in principle contribute to homoaromaticity. The above-mentioned paper, which also considered the involvement of arene oxides in the liver enzyme metabolism of aromatic molecules and in the carcinogenic action of polycyclic aromatic hydrocarbons, prompted us to study the electronic structure of molecules **1–4** and of the related molecules **5–9** (Scheme 2) by means of ultraviolet photoelectron spectroscopy (UPS) and electron transmission spectroscopy (ETS), with the aim of finding direct evidence for homoaromaticity. In particular, the UPS data, related to the filled valence orbital energies, should unveil the extent of mixing between the π system and the oxygen lone pair or σ orbitals of the three-membered ring in the epoxides. The complementary information supplied by the ETS data, related to the empty orbital energies, is of minor importance in this respect. An ETS study of these molecules does, however, constitute an independent point of interest. According to recent electron impact vibrational excitation data,[4] the first electron attachment process in cyclopropane occurs at *ca.* 2.6 eV, in spite of the fact that the ET spectrum of cyclopropane does not show evidence for temporary anion formation below 4 eV.[5] The lowest unoccupied molecular orbital (LUMO) in cyclopropane would thus lie at much lower energy than those in larger cyclic and open-chain hydrocarbons and only *ca.* 1 eV higher in energy than the π^* LUMO in ethene.[6] This exceptionally high electron affinity thus appears to be peculiar to the three-membered cycle. Although direct observation of this σ^* resonance (temporary anion formation) in ETS could be prevented by too small a cross-section, indirect evidence could arise from sizeable energy perturbations of the empty π^* orbitals in epoxides **2** and **4**, owing to strong interaction with low-energy σ^* orbitals of the epoxy ring.



Scheme 1

Experimental

ETS is one of the most suitable means for studying the virtual orbital structure of gas-phase molecular systems. This technique takes advantage of the sharp variations in the electron–molecule scattering cross-section associated with temporary electron capture into vacant orbitals. The energies (attachment energies E_{att}) at which these resonance processes occur are the negative of electron affinities. Our ETS apparatus[7] is in the format devised by Sanche and Schulz.[8] An electron beam with a typical resolution of 40 meV fwhm is passed through a collision cell containing the vapour of the



Scheme 2

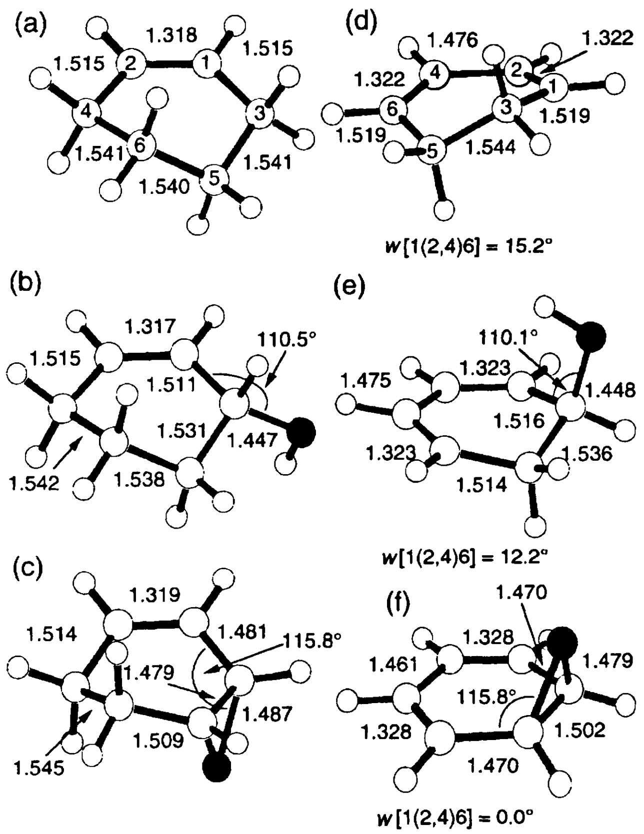


Fig. 1 Optimum geometrical structures for cyclohexene (a), **1** (b), **2** (c), cyclohexadiene (d), **3** (e) and **4** (f) computed at the HF/3-21G level; *w* represents the dihedral angle between the two C—C double bonds; bond lengths are in Å and angles in degrees

sample of interest. At energies at which electron capture into a normally unoccupied orbital occurs, there is a change in the scattering cross-section, and hence in the transmitted current. The derivative with respect to energy of the transmitted current, as a function of the incident electron energy, is recorded. The present spectra have been obtained by using the apparatus in the 'high rejection' mode, unless otherwise specified, which yields a signal related to the almost total cross-section.[9] The attachment energies given correspond to the vertical midpoints between minima and maxima in the differentiated signal. The energy scales have been calibrated with reference to the ($1s^1$ $2s^2$) anion state of He. The estimated accuracy is ±0.05 or ±0.1 eV, depending on the number of decimal digits reported.

UP spectra were obtained with a Perkin-Elmer PS18 spectrometer connected to a Datalab DL4000 signal analysis system. The spectra were calibrated using the He peak at an apparent ionisation energy (E_i) of 4.89 eV due to the small amount of the He IIα radiation in the discharge. E_i values obtained by calibration of spectra using this line, the Xe $^2P_{3/2}$ ($E_i = 12.13$ eV) and Ar $^2P_{3/2}$ ($E_i = 15.759$ eV) lines were always within ±0.01 eV, which also confirmed the linearity of the energy scale. The bands were located by using the position of their maxima, which were taken as corresponding to the vertical ionisation energies. The accuracy of the given E_i values was estimated to be ±0.05 eV. The photoelectron spectrum of compound **4** shows an unusually low intensity first band. The spectrum was run at room temperature. A total of ten spectra were obtained from two different samples, with no observable changes in the relative intensities of the bands.

Benzene oxide (**4**) was synthesized following the method reported by Paquette and Barrett.[10] 1,2-Epoxycyclohex-4-ene (**5**) and 1,2-epoxycyclohex-3-ene (**2**) were prepared according to the procedure described by Fringuelli *et al.*[11] Benzene hydrate (**3**) was obtained by reduction of 1,2-epoxycyclohex-3-ene (**2**) with $LiAlH_4$, as reported in the literature.[12] Analyses on the purity of the products were performed by means of gas-chromatograph mass spectrometry and 200 MHz NMR spectroscopy. Compounds **1** and **6–9** were commercially available.

Computations

Hartree–Fock *ab initio* computations were carried out on cyclohexene, cyclohexadiene and on the corresponding alcohols and epoxides **1**, **2**, **3** and **4** with the Gaussian 92/DFT[13] series of programs using the 3-21G[14] basis set. In all cases, the geometries of the various structures were fully optimised with the gradient method available in Gaussian 92. The nature of each critical point was characterised by computing the harmonic vibrational frequencies. For the molecular systems **1**, **2** and **3**, the two possible isomers which correspond approximately to an axial or equatorial orientation of the C—O bonds have been considered; here only the results obtained for the more stable isomers are reported. The optimum structures, together with the values of the most relevant geometrical parameters, are represented in Fig. 1. The energy values calculated for the frontier molecular orbitals are given in Table 1.

Results and Discussion

Alkenes

The UP and ET spectra of the cyclohexene derivatives **1** and **2** and of related unsaturated and saturated molecular systems are presented in Fig. 2 and 3, respectively. The corresponding frontier MO structures in these molecules are reported in Fig. 4, which displays the measured E_{att} and E_i values. Homoaromaticity in benzene oxide (**4**) implies the participation of the oxygen lone pair (n_o) orbital or of the filled σ_{co} orbitals in the π system, with consequent n_o–π mixing and σ_{co}–π mixing. The series of cyclic monoenes **1**, **2** and **5** is suitable for evaluating the extent of these two relevant interactions, or at least their relative extents in the alcohol and epoxide derivatives. Replacement of a hydrogen atom adjacent to the double bond

Table 1 Frontier orbital energies supplied by 3-21G *ab initio* calculations

	molecule					
orbital	cyclohexene	**1**	**2**	cyclohexadiene	**3**	**4**
π^*	5.41	4.86	4.35	—	—	—
π	−9.32	−9.67	−9.45	—	—	—
n_o	—	−11.26	−12.03	—	−11.25	−11.83
σ	−11.64	−12.12	−11.63	—	—	—
π_-^*	—	—	—	7.16	6.90	5.77
π_+^*	—	—	—	3.71	3.24	2.83
π_-	—	—	—	−8.24	−8.74	−8.93
π_+	—	—	—	−11.53	−12.01	−10.8
						−13.5

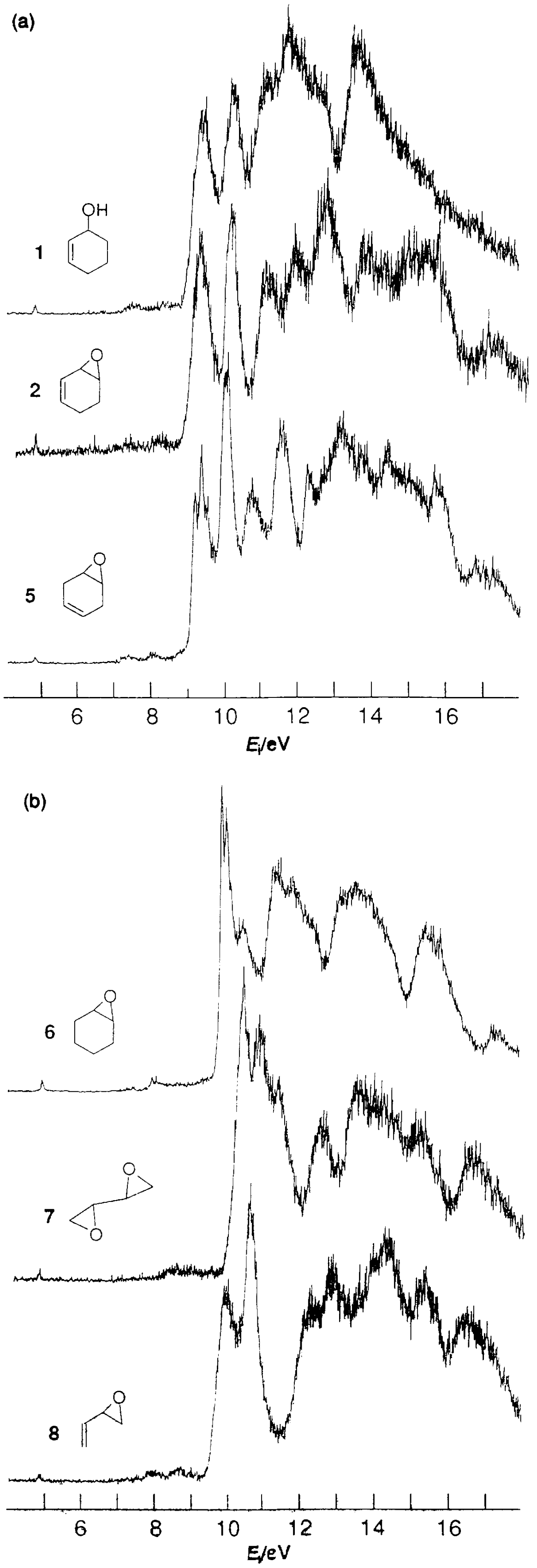


Fig. 2 (a) He I photoelectron spectra of cyclohex-2-en-1-ol(**1**), 1,2-epoxycyclohex-3-ene (**2**) and 1,2-epoxycyclohex-4-ene (**5**); (b) He I photoelectron spectra of cyclohexene oxide (**6**), 1,2,3,4-diepoxybutane (**7**) and 3,4-epoxy-1-butene (**8**),

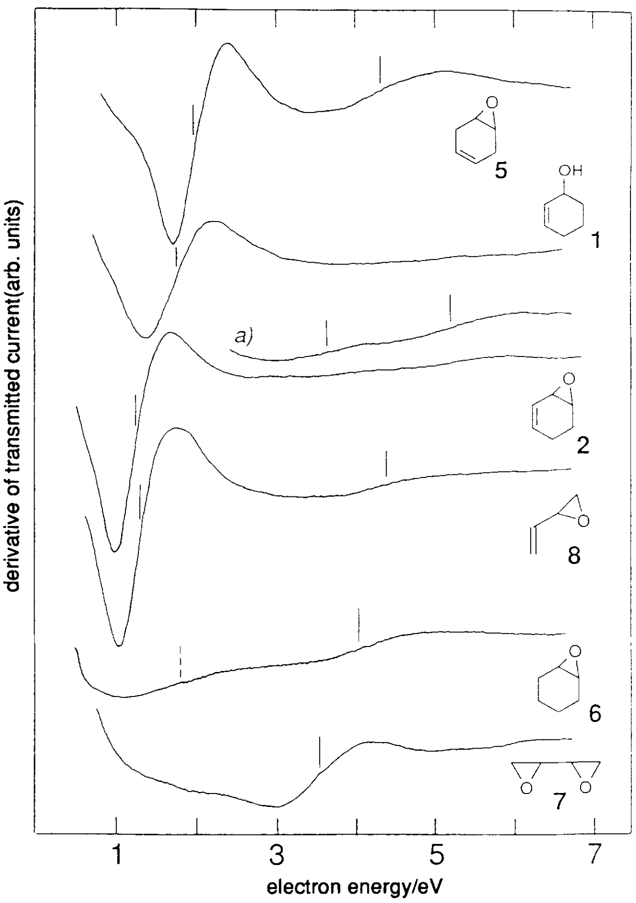


Fig. 3 Derivative of the electron current transmitted through the vapours of 1,2-epoxycyclohex-4-ene (**5**), cyclohex-2-en-1-ol (**1**), 1,2-epoxycyclohex-3-ene (**2**), 3,4-epoxy-1-butene (**8**), cyclohexene oxide (**6**) and 1,2,3,4-diepoxybutane (**7**), as a function of the incident electron energy. Vertical lines locate the most probable E_{att} values. (*a*) Spectrum recorded in the "low-rejection" mode (see text).

with an OH group in cyclohexene causes a 0.2 eV stabilisation of the π highest occupied molecular orbital (HOMO). This indicates a prevailing inductive effect of the substituent, given that n_o–π and σ_{co}–π mixing would act in the opposite direction. On going from the alcohol **1** to either the corresponding epoxide **2** or to the epoxide isomer **5**, where the fused three-membered ring is displaced on the opposite side with respect to the double bond, the energy of this π orbital remains constant within experimental error. This suggests that even when the epoxide ring is adjacent to the double bond, the filled π orbital is not significantly affected by interaction with either the oxygen lone pair or with the σ_{co} orbitals. These indications are confirmed by the energies of the second highest occupied orbital, which possesses mainly oxygen lone pair character. On going from the saturated derivative **6** to the unsaturated epoxides **2** and **5**, the presence of the C=C double bond causes a slight stabilisation of the n_o orbital. There is no evidence of n_o–π mixing in **2**, which would result in a sizeable stabilisation of the n_o orbital with respect to **5**, where this interaction is prevented by the large distance between the oxygen atom and the double bond. Comparison with the energy of the n_o orbital in alcohol **1** leads to the same conclusion. Analogous considerations apply when the filled valence orbitals of the ethene derivative **8** are considered (Fig. 4). The energy of the oxygen lone pair orbital coincides with the baricentre of the corresponding orbitals in the saturated reference molecule **7**, thus indicating the absence of significant n_o–π mixing. The hyperconjugative destabilisation (0.6 eV) produced by the cyclic substituent on the ethene π HOMO in **8** is similar to that caused by a methyl group (0.5 eV[17]), suggesting that mixing of the π orbital with the σ orbitals of the three-membered ring is not particularly operative.

As opposed to the near-constancy of the π HOMO energy in the cyclic monoenes, the ET spectra show that the energy of

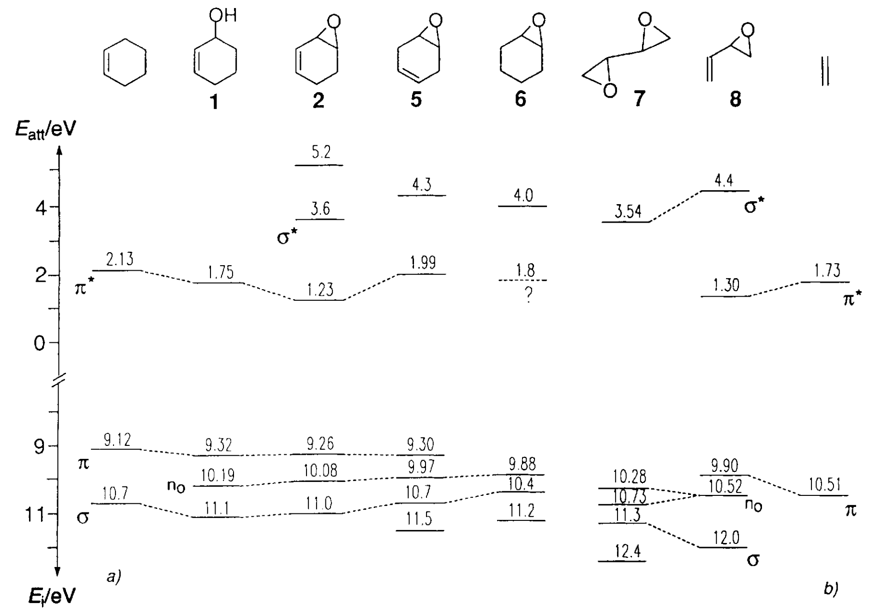


Fig. 4 E_i and E_{att} values measured in cyclohexene, cyclohex-2-en-1-ol (**1**), 1,2-epoxy cyclohex-3-ene (**2**), 1,2-epoxycyclohex-4-ene (**5**), cyclohexene oxide (**6**), 1,2,3,4-diepoxybutane (**7**) and 3,4-epoxy-1-butene (**8**). (*a*) E_i and E_{att} values taken from ref. 15 and 24, respectively. (*b*) E_i and E_{att} values taken from ref. 16 and 21, respectively.

the π^* LUMO undergoes sizeable changes along the series (see Fig. 4). On going from the unsubstituted cyclohexene to the epoxy derivative **5**, the π^* empty orbital experiences only a small inductive stabilisation, in line with the corresponding E_i data related to the filled counterpart. Note that, in addition to being due to the large distance, n_o–π^* mixing is also forbidden for symmetry reasons. The further 0.24 eV stabilisation of the π^* LUMO on going from the epoxide **5** to the alcohol **1** can be explained in terms of mixing of the π^* orbital with an empty σ^*_{co} orbital lying higher in energy.

It is not surprising that the corresponding σ^* resonance is not observed in the ET spectrum. Temporary anionic states associated with unoccupied σ^* orbitals, owing to their usually high energy and low potential barrier, generally have a short lifetime, thus giving rise to broad and weak resonances. Previous ET investigations in hydrocarbons containing Group 16 elements[18–23] have shown that low-energy σ^* resonances with mainly heteroatom character are present in sulfur (or heavier atom) derivatives, but not in oxygen derivatives. In the epoxy derivative **2** the effect of π^*–σ^* mixing is greatly enhanced. On going from 2-cyclohexen-1-ol **1** to the corresponding epoxide **2**, a sizeable electron affinity increase (0.52 eV) is observed. The π^* LUMO in **2** is 0.9 eV more stable than that in the unsubstituted cyclohexene and this large effect is mainly due to strong interaction of the π^* orbital with σ^* orbitals of the epoxy group. In agreement, the ET spectrum of **2** displays a second feature at 3.6 eV, rather broad and weak but not present in cyclohexene or in the -OH derivative **1**, and which should be associated with an empty σ^* orbital of the epoxy group mixed with the π^* LUMO. This resonance is more visible in the ET spectrum recorded in the "low-rejection" mode, reported in Fig. 3, where the signal is related to the back scattering cross section.[9] These findings are therefore consistent with the electron impact vibrational excitation data of Allan[4] mentioned in the introduction, according to which cyclopropane possesses a low-lying (2.6 eV) σ^* orbital, the second resonance (also observed in ETS) lying at about 5.5 eV.

In our molecular system where the σ frame is more extended and an electronegative oxygen atom is present, the lowest σ^* orbitals (before mixing with the π^* LUMO) could lie at even lower energy than those in cyclopropane. However, according to the nodal and localisation properties suggested for the empty orbitals associated with the two resonances in cyclopropane,[4] this stabilising effect should affect the second LUMO to a larger extent, that is, a $\sigma^*(a'_2)$ C—C antibonding orbital mainly localised on the carbon skeleton. In contrast, the reduction in the number of C—H bonds, due to substitution of a CH_2 group with an oxygen atom and of two C—H bonds with C—C bonds, could also perturb, in the opposite direction, the cyclopropane LUMO (a''_2), described as an in-phase combination among σ^*_{C-H} fragment orbitals. These qualitative considerations are supported by the energy shifts of the two resonances on going from cyclopropane to ethene oxide:[25] the first resonance is destabilised to 2.8 eV, while the second one is stabilised to 4.6 eV. In epoxide **5** no resonance corresponding to the σ^* resonance at 3.6 eV in **2** is observed. The weak σ^* resonance could be located close in energy to the π^* resonance centred at 1.99 eV and could thus be hidden by this intense signal. It is also true that in the absence of σ^*–π^* mixing, the σ^* orbital could possess such a large *s*-wave contribution (and consequently such a short lifetime) to render its observation difficult. This could be the case for **5** as well as for cyclopropane, whose ET spectrum[5] does not show low-energy resonances. Unfortunately, the ET spectrum of the saturated cyclohexene oxide (**6**) does not provide clear insight in this regard. It displays, in fact, a variation in the derivative of the scattering cross-section centred at about 1.8 eV. This signal, however, is probably too broad and weak to be assigned with certainty to resonant scattering from the LUMO rather than to a fluctuation in the potential scattering background. For this reason this signal is represented with a dashed line and a question mark in Fig. 4.

The second feature, centred at 4.0 eV, likely corresponds to the resonance observed at 4.6 eV in ethene oxide by Allan.[25] Even the ET spectrum of buta-1,3-diene diepoxide (**7**) does not supply any direct evidence for a resonance below 3 eV. The first feature observed is in fact located at 3.54 eV, leaving the doubt as to whether this resonance is to be associated with the LUMO or whether a large *s*-wave contribution to the scattering cross-section for the LUMO prevents its observation at lower energy. The presence of a resonance at 2.8 eV in ethene oxide would favour the latter hypothesis.

Finally, in butadiene monoxide (**8**), the π^* LUMO lies at 0.43 eV lower energy than in ethene (see Fig. 4). The increase in electron affinity caused by the epoxy substituent is smaller than that measured in the cyclohexa analogue **2**. This could be due to either overlap or energy reasons: the conformation assumed by the open-chain molecule **8** could reduce the σ^*–π^* overlap, and the energy gap between the σ^* and π^* interacting orbitals is probably smaller in **2**. In fact, the larger σ framework should stabilise the lowest-lying σ^* MO and destabilise the π^* MO (as indicated by comparison between the π^* E_{att}s in cyclohexene and ethene). The frontier orbital energies supplied by *ab initio* 3-21G calculations for cyclohexene and its derivatives **1** and **2** are reported in Table 1. The energy trends calculated for the π HOMO and, less expectedly,[26] for the π^* LUMO are in excellent (also quantitative) agreement with the measured ionisation energy and attachment energy values, respectively. In particular, on going from cyclohexene to the hydroxy derivative, both the filled π and the empty π^* orbitals are predicted to be stabilised, the latter to a slightly larger extent. On going from the hydroxy to the epoxy derivative a small destabilisation is predicted for the HOMO, whereas for the LUMO a sizeable stabilisation (0.51 eV) is predicted. According to the calculated localisation properties, the contribution to the HOMO from the substituent is similar and small in both the alcohol and the epoxide. The agreement between calculated orbital energies and experiment becomes worse when the next occupied orbitals are considered. For the epoxy derivative the calculations predict an energy splitting smaller than 0.4 eV between the second occupied orbital (mainly localised at the C—O bonds) and the third occupied orbital (with mainly n_o character). The latter would thus be *ca.* 0.8 eV more stable than the corresponding orbital in alcohol **1**. These results are not supported by the photoelectron spectra.

Dienes

Fig. 5 and 6 report the UP and ET spectra, respectively, of cyclohexa-1,3-diene hydroxy (**3**) and epoxy (**4**) derivatives and of cycloheptatriene (**9**). The E_i and E_{att} values measured in these compounds are given in Fig. 7. On going from cyclohexa-1,3-diene to **3**, both the filled and empty π orbitals are stabilised by about 0.3 eV, the energy separations between the in-phase and out-of-phase combinations remaining almost unchanged. The effects produced by replacement of a hydrogen atom with an OH group at a carbon atom adjacent to the π system are quite similar to those observed in the corresponding alkenes. In addition the E_i value from the oxygen lone pair is close to that measured in **1**.

Before discussing the frontier energy levels of benzene oxide (**4**), the possibility that this rather unstable molecular system can isomerise to oxepin in the gas phase must be considered. Oxepin is the seven-membered cyclotriene deriving from cleavage of the fused C—C bond in benzene oxide. Measurements of the temperature dependence of the equilibrium constants for the benzene oxide ↔ oxepin reaction in a non-polar solvent by Vogel and Günter[28] lead to an enthalpy of isomerisation of 1.7 kcal mol^{-1} and to a Gibbs energy of isomerisation of -1.3 kcal mol^{-1} at room temperature. In the gas phase, according to MINDO/3 calculations, oxepin should be more stable and the equilibrium should be shifted toward this isomer.[29] The thermodynamically less stable benzene oxide could be kinetically quite stable, provided the activation energy is sufficiently large. According to the same MINDO/3 calculations cited above, however, this would not be the case, the calculated activation energy (*ca.* 12 kcal mol^{-1}) suggesting a rather rapid conversion. In spite of this prediction, the present spectroscopic data (in particular the UP spectrum), indicate that a single compound is present in the gas phase, whose filled electronic structure is not consistent with the four (three ethene double bonds plus the oxygen lone pair) conjugated π orbitals of oxepin. The HOMO of oxepin should derive from the HOMO of cyclohepatriene (**9**), that is, the

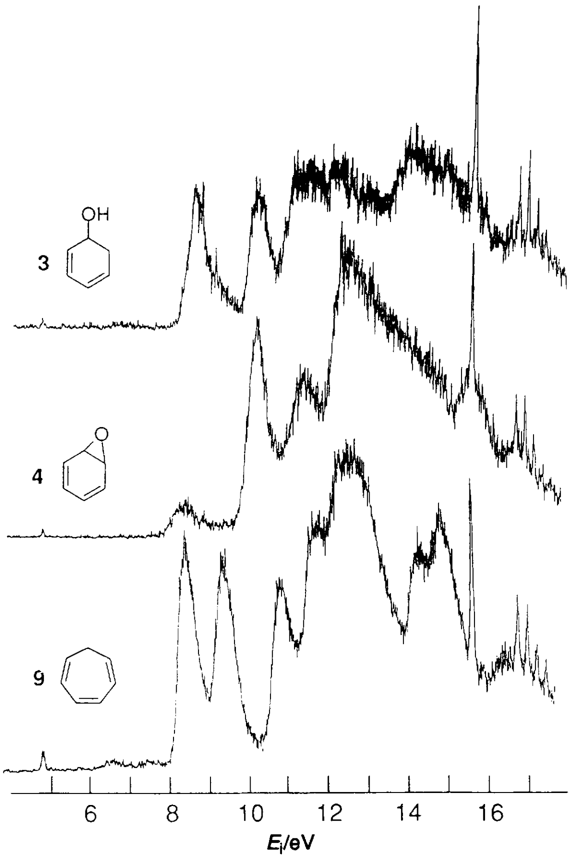


Fig. 5 He I photoelectron spectra of benzene hydrate (**3**), benzene oxide (**4**) and cycloheptatriene (**9**)

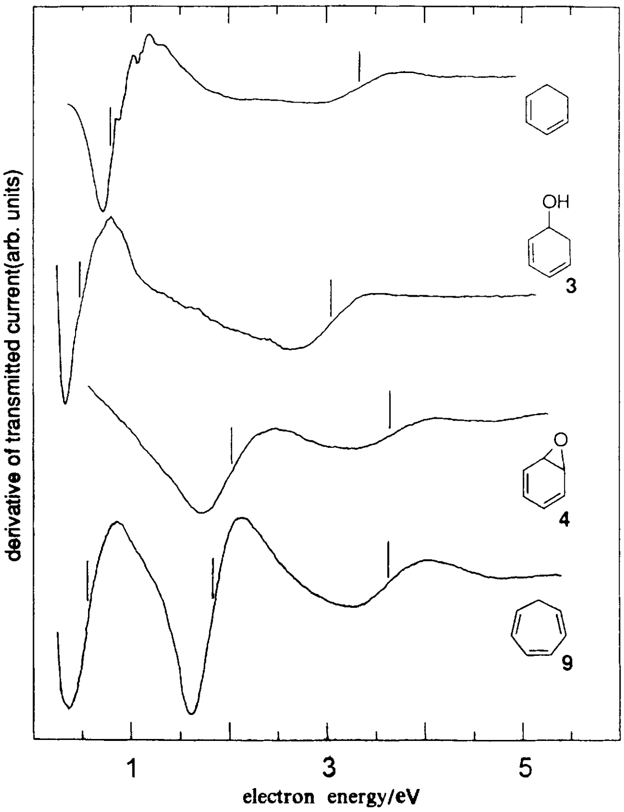


Fig. 6 Derivative of the electron current transmitted through the vapours of 1,3-cyclohexadiene, benzene hydrate (**3**), benzene oxide (**4**) and cycloheptatriene (**9**), as a function of the incident electron energy. Vertical lines locate the most probable E_{att} values.

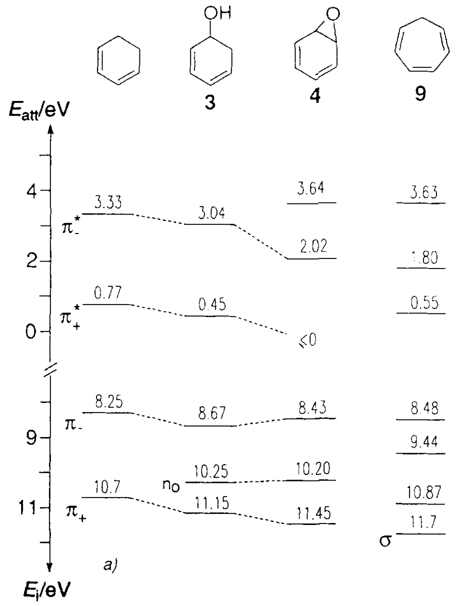


Fig. 7 E_i and E_{att} values measured in 1,3-cyclohexadiene, benzene hydrate (**3**), benzene oxide (**4**) and cycloheptatriene (**9**). (*a*) E_i values taken from ref. 27.

antibonding combination of the three ethene fragment π orbitals, destabilised by mixing with the lower-lying oxygen lone pair. The second occupied orbital should essentially be the antisymmetric non-bonding combination of the ethene π orbitals (9.44 eV in **9**), which, by symmetry, cannot mix with the oxygen lone pair. On the contrary, the HOMO in compound **4** is not significantly destabilised with respect to **9** and no signal is observed in the energy range where the second occupied orbital of oxepin should fall. In contrast, the UP spectrum, which is not much different from that of the alcohol **3**, is consistent with the electronic structure of benzene oxide, displaying only three peaks below 11.5 eV.

The second occupied MO in **4** ($E_i = 10.20$ eV) lies at only slightly higher energy than that in the hydroxy analogue, as well as those in the corresponding alkenes, and is assigned to the oxygen lone pair. The π_- and π_+ MOs are symmetrically shifted to higher and lower energy, respectively, on going from the alcohol to the epoxide, so that their energy separation is 0.54 eV larger in the latter. This finding cannot be explained in terms of n_o–π interaction, because mixing between the antisymmetric π_- MO and the oxygen lone pair is symmetry forbidden. The E_i data seem also to rule out any sizeable mixing of the π system with the lower-lying σ_{co} orbitals of the epoxy group. This interaction, in fact, should mainly perturb the π_+ combination, which is much closer in energy to the σ_{co} orbitals than the π_- combination, and would cause a larger destabilisation of the former. Thus, the concomitant stabilisation of the π_+ MO and destabilisation of the π_- MO on going from **3** to **4** does not constitute any evidence for participation of the oxygen lone pair or of the σ orbitals of the fused three-membered cycle to the π butadiene system; it would rather be consistent with geometrical effects, that is, a larger coplanarity and/or shorter distance (and thus increased extent of interaction) between the two ethene π orbitals in benzene oxide. The calculated geometries support this interpretation and predict the occurrence of both factors: on going from the hydroxy to the epoxy derivative the dihedral angle between the two double bonds decreases from 12.2 to 0.0° and the C—C bond length between them is reduced from 1.475 to 1.461 Å (see Fig. 1)). The present results, therefore, argue against homoaromaticity in benzene oxide, in agreement with the conclusions drawn by comparing the calculated bond lengths with those of butadiene.[29]

The ET spectra, in line with the results obtained for the alkene analogues, show that the epoxy group brings sizeable energy perturbations on the empty π* levels. The ground anionic state of benzene oxide is thus stable or close to zero energy, where it would be hidden by the intense electron beam signal. The first resonance observed in the spectrum lies at 2.02 eV, and is assigned to the π_-^* MO with a strong σ* contribution. Mixing with σ* orbitals, in fact, not only counterbalances the destabilisation due to geometrical effects (as observed for the filled counterpart) but stabilises the π_-^* MO to 1 eV lower energy with respect to the corresponding orbital in the alcohol **3**. The second resonance displayed in the ET spectrum of **4** (3.64 eV) is associated with a σ* MO with large π* character, as confirmed by its relatively high intensity and sharpness when compared to σ* resonances in this energy range. Owing to the experimental evidence for such strong mixing, it would probably be more meaningful to point out the π*–σ* nature of both these MOs, rather than labelling the first as a π* and the second as a σ* MO. It is not clear whether the resonance at 3.64 eV is due to a single orbital (antisymmetric with respect to a plane perpendicular to the three-membered ring) or whether it also contains some unresolved contribution from a symmetric σ* MO mixed with the π_+^* LUMO. However, such symmetric σ* resonance is probably too broad to be detected because of a smaller π* character and a larger s-wave contribution. As already noted for the corresponding alkenes, the orbital energies calculated for cyclohexadiene and its hydroxy and epoxy derivatives **3** and **4** closely reproduce the experimental trends, except for the filled orbitals in benzene oxide (see Table 1). The energy separation between the in-phase and out-of-phase combinations of both the filled π and the empty π* orbitals of cyclohexadiene is overestimated by almost 1 eV. However, the calculations correctly predict that all four π orbitals are stabilised by 0.3–0.5 eV through replacement of an H atom with an OH group. On going from the hydroxy derivative **3** to benzene oxide **4**, the LUMO (π_+^*) is predicted to be stabilised by 0.4 eV, confirming that the ground anion state (not observed in the ETS spectrum) lies close to zero energy. The stabilisation energy calculated for the second empty orbital (π_-^*) is much larger (1.13 eV), in quite good agreement with experiment. The localisation properties calculated for the π_-^* MO confirm a strong contribution from σ* (C—O) orbitals. When the filled orbitals of benzene oxide are considered, the discrepancies between the calculated orbital energies and the photoelectron spectrum are apparent. As well as in the case of the corresponding alkene **2**, the origin of the discrepancy can be traced back to the overestimation of the energy of a σ_{co} orbital. In benzene oxide this orbital would fall very close in energy to the π_+ orbital, with the proper symmetry to mix with it. The calculations thus predict two delocalised π_+–σ_{co} molecular orbitals resulting from this strong interaction, split in energy by 2.8 eV. The outermost would be the second occupied orbital and would lie 0.8 eV above the n_o orbital, in contrast with experiment.

Conclusion

The filled valence electronic structures in gas-phase unsaturated cyclohexaderivatives, as deduced by means of photoelectron spectroscopy, indicate that the localised orbitals of hydroxy and epoxy substituents do not mix significantly with adjacent π orbitals. The lack of evidence for participation of the oxygen lone pair and of filled σ_{co} orbitals in the π system in the epoxy derivatives, as well as in the hydroxy derivatives, does not support the hypothesis of homoaromaticity in arene oxides. In particular, the present results imply that the small rate of acid-catalysed aromatisation for benzene oxide cannot be ascribed to homoaromatic stabilisation of the reactant. As opposed to the small and similar energy perturbations caused by the hydroxy and epoxy substituents on the filled π orbitals, the electron transmission spectra show that the empty π^* orbitals are affected to very different extents by the two substituents. The epoxy group, in fact, causes a large stabilisation of the π^* LUMO (that is, a large electron affinity increase) in the molecular systems considered. This finding suggests that the three-membered cycle possesses empty σ^* orbitals lying at low energy with respect to other saturated molecular systems and that there is a strong mixing of these σ^* orbitals with adjacent empty π^* orbitals.

The agreement between these computations at the Koopmans' theorem level and experiment is not completely satisfactory. This is to be expected and to go beyond this level for molecules of this size would be a major computational task.

A.M. and F.S. thank the Italian Ministero dell'Universtà e della Ricerca Scientifica e Tecnologica for financial support. The authors are grateful to Dr. Michael Allan for helpful discussion and to Laura Favaretto for technical assistance in the analytical tests of the products.

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Paper 5/06962I; *Received* 23*rd October*, 1995