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Gas-Phase Generation and Structural Characterization of $[H_2, C, O, Si]^{\bullet+}$ and $[H_2, C, O, Si]$ by Collisional-Activation and Neutralization-Reionization Mass Spectrometry and Theory: Evidence for the Distonic Ion $H_2C^{\bullet}{-}O{-}Si^{+}$ and the Biradical $H_2O^{\bullet}{-}O{-}Si^{\bullet}$

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Abstract: Results of laboratory measurements and theoretical investigations are reported which provide evidence for the stability of the distonic ion $^{\bullet}CH_2OSi^{+}$ and which show that the biradical species $^{\bullet}CH_2OSi^{\bullet}$ may be generated by the neutralization of the distonic ion *in the gas phase*. The measurements were made using collisional-activation and neutralization-reionization mass spectrometry. Ions of the type $[H_2, C, O, Si]^{\bullet+}$ were generated by electron-impact ionization of $Si(OCH_3)_4$ at 70 eV. Observed collisional-activation (CA) mass spectra of these ions at 8-keV translational energy are most compatible with the connectivity $^{\bullet}CH_2OSi^{+}$. Neutralization-reionization (NRMS) experiments with this distonic ion suggest an identical connectivity for the corresponding neutral species. The experimental findings are complemented by ab intio MO studies (MP2/6-31G**//MP2/6-31G** +ZPVE) which predict that the heavy-atom backbone of both the distonic ion and the biradical neutral are linear and that they have very similar bond lengths. They also provide useful information on the energetics of the unimolecular decompositions of the distonic ion and the energetics and structures of many of its isomers.

Introduction

Collisional-activation (CA) and neutralization-reionization (NR) mass spectrometry together provide a powerful technique for the interrogation of structural features of related ions and molecules, particularly if these species are inherently reactive so that they cannot easily be isolated and investigated with other techniques.[1,2] Small unusual silicon-containing molecules and ions provide a case in point. Recently such species have become the subject of considerable theoretical scrutiny,[3,4] and the laboratory investigation of their chemistry in the gas phase has become topical.[5] In reponse to a need for more experimental information on the structures of these species, we initiated systematic CA and NRMS investigations of silicon species which early on were focused on silicon-containing ions and molecules with one other heteroatom, viz. ions and neutrals with the composition $[H_n, O, Si]$ with $n = 1$–3,[6,7] $[H_n, C, Si]$ with $n = 1$–3,[8] and $[H_n, C_2, Si]$ with $n = 1$ and 2.[9,10] Here we report the results of a detailed experimental and theoretical investigation of a silicon species containing both oxygen and carbon as heteroatoms, $[H_2, C, O, Si]$. In particular, this investigation was directed to the possible experimental generation and identification of the novel, interesting distonic[11] ion $^{\bullet}CH_2OSi^{+}$ and its neutralization to produce the unusual biradical species $^{\bullet}CH_2OSi^{\bullet}$.

The interest in neutral molecules of composition $[H_2, C, O, Si]$ has come largely from extraterrestrial chemistry of $Si^{\bullet+}$ in which it has been proposed to be formed from $SiOCH_3^{+}$ by recombination with electrons or proton transfer with a molecule M, as shown in reaction 1.[5] The $SiOCH_3^{+}$ may be derived by O–H bond insertion from reaction 2b and by the chemical sequence given by reactions 2a and 3.[12] To the extent that trace amounts of methanol are present, this chemistry should also be operative in the earth's ionosphere where it will serve as a sink for $Si^{\bullet+}$ produced by meteoric ablation.

$$SiOCH_3^{+} + e^{-}\,(M) \rightarrow SiOCH_2 + H^{\bullet}\,(MH^{+}) \qquad (1)$$

$$Si^{\bullet+} + CH_3OH \rightarrow SiOH^{+} + CH_3^{\bullet} \qquad (2a)$$

$$Si^{\bullet+} + CH_3OH \rightarrow SiOCH_3^{+} + H^{\bullet} \qquad (2b)$$

$$SiOH^{+} + CH_3OH \rightarrow SiOCH_3^{+} + H_2O \qquad (3)$$

Silaketen, $H_2Si{=}C{=}O$, is the only isomer of the biradical $^{\bullet}CH_2OSi^{\bullet}$ which has been the subject of a theoretical investigation[13] in connection with matrix isolation experiments which attempted to make and detect dimethylsilaketene.[14] Theoretical investigations of other isomers, particularly of the biradical $^{\bullet}CH_2OSi^{\bullet}$ itself, apparently have not been reported previously. Furthermore, the ions of these molecules appear never to have been investigated with theory.

In contrast, neutral isomers of the carbon analogue $[H_2, C_2, O]$ and their radical cations have been thoroughly examined with

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state-of-the-art ab initio molecular orbital calculations.[15,16] However, in this case, calculations on the distonic ion, $^{\bullet}CH_2OC^+$, and the corresponding biradical neutral, $^{\bullet}CH_2OC^{\bullet}$, have not been reported. A previous experimental CA and NRMS study has demonstrated the generation and characterization of an isomer of ketene, viz. hydroxyacetylene, $HC{\equiv}COH$, and its radical cation, as well as the radical cation of the well-known ketene molecule.[17]

Experimental Section

The experiments were performed with a substantially modified ZAB-HF mass spectrometer which has been described in detail previously.[6,7,10] The facility is a four-sector mass spectrometer with BEBE configuration, where B denotes a magnetic and E an electric sector. Positive ions $[H_2, C, O, Si]^{\bullet+}$ were generated by the ionization of tetramethoxysilane with 70-eV electrons. The ion source conditions were as follows: ion trap current, 100 μA; emission current in chemical ionization mode, 500 μA; ion source temperature, 200 °C; mass resolution, $m/\Delta m$, 1500 (10% valley definition).

Collisional activation[1] used to characterize the ions leaving the source was achieved by mass-selecting the 8-keV ion beam by means of B(1)-E(1) and colliding it, in the case of the positive ions, in the collision chamber located in the third field-free region (He, 80% transmittance, *T*). Ionic products were recorded by scanning B(2). In the NRMS experiments[2] the 8-keV beam of positive ions was neutralized with xenon (80% *T*) in the first of two differentially pumped collision cells located in the field-free region between E(1) and B(2). Unreacted ions were deflected away from the beam of neutral species by applying a voltage of 1000 V on the deflector electrode. Subsequent reionization occurred in the second collision cell by collision with oxygen (70% *T*). The resulting mass spectra were recorded by scanning B(2). The minimum lifetime *t* (equal to the transit time between the two collision cells) is of the order of 1 μs.

In all experiments, signal-averaging techniques were used to improve the *S/N* ratio. The data were accumulated by on-line processes using an AMD-Intectra computer system DP 10.

Theoretical Section

The lack of theoretical studies for the species $[H_2, C, O, Si]^{\bullet+}$ prompted us to perform a thorough theoretical investigation of the structure and energies of the isomers of this species. The details of this investigation are reported elsewhere,[18] but here we present results which complement the experimental investigation.

All molecular orbital calculations were performed with the GAUSSIAN 88 program package,[19] in which the open-shell systems are treated in the unrestricted Hartree–Fock (UHF) formalism.[20] The geometries were fully optimized (irrespective of all restrictions arising from symmetry) using analytical gradient procedures. All stationary points have been characterized to respond to local minima or transition structures by having zero or one, and only one, negative eigenvalue in the analytically computed Hessian force constant matrix. The notation 6-31G*//6-31G* means that the structure was optimized with the polarized 6-31G* set[21] and the same basis set was used for the computation of the zero-point vibrational energy (ZPVE) from the harmonic frequency. The ZPVE was scaled by a factor of 0.89 in order to account for the systematic overestimation of normal frequencies by Hartree–Fock calculations.[22] The geometry of significant points was reoptimized with the 6-31G** basis set[23] by accounting for the effect of electron correlation with second-order Møller–Plesset perturbation theory (MP2).[24] This level of calculation has been denoted as MP2/6-31G**//MP2/6-31G** and if the energy is corrected for ZPVE, should be suitable for the description of the structures and energetics of the systems of interest in this study.[4,25,26]

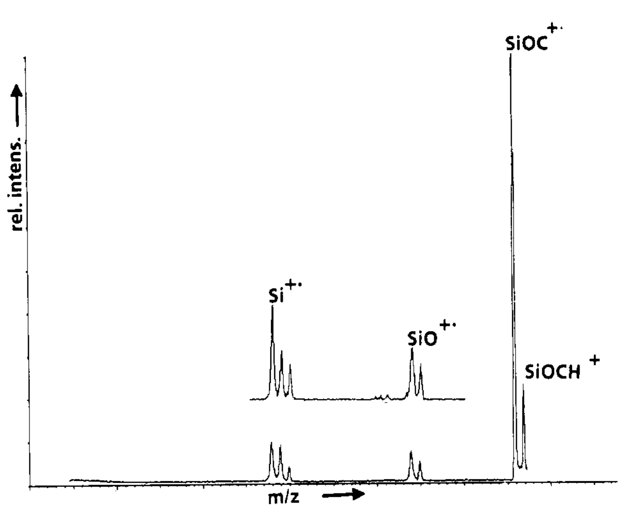

Figure 1. CA mass spectrum (He, 80% *T*) of *m/e* 58 $[H_2, C, O, Si]^{\bullet+}$ generated from $Si(CH_3O)_4$ by electron impact.

Results and Discussion

The observed metastable ion decompositions of $Si(OCH_3)_4^{\bullet+}$ (*m/z* 152) indicate sequential losses of three molecules of formaldehyde and two of molecular hydrogen. These results lead to the expectation that the connectivity CH_2–O–Si present in the tetramethoxysilane molecule chosen as parent is likely to be preserved in the daughter ion at *m/z* 58 produced by the electron-impact ionization at 70 eV.[27] There is other evidence for such retention of connectivity for the ions $SiOCH_3^+$ and $HSiOCH_3^{\bullet+}$, for example, when these are derived by electron impact of tetramethoxysilane.[28] Also, formaldehyde loss from similar methoxy-substituted silane cations has been reported in the literature.[29] Accurate mass measurements indicated that the ion at *m/z* 58 derived from tetramethoxysilane by electron impact has the elemental composition $[H_2, C, O, Si]$ and not $[C_2, H_2, O_2]$ or $[C_4, H_{10}]$. The CA spectrum of the ion with the elemental composition $[H_2, C, O, Si]$ is shown in Figure 1. Intense fragments are observed at *m/z* 57, $[H, C, O, Si]^+$, 56 $[C, O, Si]^{\bullet+}$ (the base peak), 45 $[H, OSi]^+$, 44 $(SiO^{\bullet+})$, 30 $[H_2, CO]^{\bullet+}$ or $(SiH_2^{\bullet+})$, 29 $[H, CO]^+$ or (SiH^+), and 28 $(CO^{\bullet+})$ or $(Si^{\bullet+})$ corresponding to loss of $H^{\bullet}$, H_2 (predominant), $CH^{\bullet}$, CH_2, Si or CO, $SiH^{\bullet}$ or $CHO^{\bullet}$, and SiH_2 or CH_2O, respectively, where the assumption is made that the atoms leave as bound molecules when possible. Much weaker signals are evident in the CA spectrum at *m/z* 42 $[H_2, CSi]^{\bullet+}$, 41 $[H, CSi]^+$, 40 $(CSi^{\bullet+})$, 16 $(O^{\bullet+})$, 14 $(CH_2^{\bullet+})$, 13 (CH^+), and 12 $(C^{\bullet+})$ corresponding to loss of O, $OH^{\bullet}$, H_2O, $[H_2, CSi]$, SiO, $[H, OSi]^{\bullet+}$, and $[H_2, OSi]$, respectively.

In analyzing the CA spectrum shown in Figure 1, we may note first the intense peaks at *m/z* 44 and 45 which require the connectivity SiO and arise from the loss of CH_2 and $CH^{\bullet}$, respectively, as well as the intense peaks at *m/z* 28, 29, and 30 which require

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Table I. Calculated and Experimental Energies (kcal mol^{-1}) for the Dissociation of the Distonic Ion $^{\bullet}CH_2OSi^+$ (Energies Are Equal to the Differences in Energy between the Final and Initial States and Do Not Include Possible Contributions Due to Intermediate Energy Barriers)

products	ΔE_{calc}[a]	ΔH_{expl}[b]
$SiOC^{\bullet+} + H_2$	54.3	
$SiOH^+ + CH^{\bullet}$	102.1	93
$SiOH^{\bullet} + CH^+$	207.2	
$SiO^{\bullet+} + CH_2$	144.5	132
$SiO + CH_2^{\bullet+}$	108.1	106
$SiH_2^{\bullet+} + CO$	46.8	49
$SiH_2 + CO^{\bullet+}$	163.7	165
$SiH^+ + HCO^{\bullet}$	78.4	82
$SiH^{\bullet} + HCO^+$	82.6	86
$Si^{\bullet+} + H_2CO$	68.1	(68.1)[b]
$Si + H_2CO^{\bullet+}$	139.9	132

[a] Calculated at the MP2/6-31G** level of theory and not corrected for ZPVE. [b] Dissociation enthalpies based on experimental enthalpies of formation available in ref 30 except for the experimental enthalpy of formation of $SiOH^+$ which was taken from ref 31. Since the absolute enthalpy of formation of the distonic ion $^{\bullet}CH_2OSi^+$ is not known, the calculated energy of dissociation of the distonic ion into $Si^{\bullet+} + H_2CO$ is used as a benchmark for deriving the dissociation enthalpy, ΔH_{expl}, by using the following equations: $\Delta H_f(^{\bullet}CH_2OSi^+) = [\Delta H_f(Si^{\bullet+}) + \Delta H_f(CH_2O] - 68.1$; $\Delta H_{expl} = [\Delta H_f(A^+) + \Delta H_f(B)] - \Delta H_f(^{\bullet}CH_2OSi^+)$.

the connectivity CO and arise from either the loss of SiH_2, $SiH^{\bullet}$, and Si (giving rise to $CO^{\bullet+}$, CHO^+, and $CH_2O^{\bullet+}$) or the loss of CH_2O, $CHO^{\bullet}$, and CO (giving rise to $Si^{\bullet+}$, SiH^+, and $SiH_2^{\bullet+}$). These observations establish a connectivity for the heavy-atom backbone given by C–O–Si, either acyclic or cyclic, if one isomer predominates at *m/z* 58. The acyclic structure is more likely for at least two reasons. The weakness of the signals corresponding to $SiCH_n^+$ for $n = 0$–2 indicates an open structure. Also, theory suggests that an open structure is more stable—the lowest stable cyclic isomer, $[c\text{-}HCOSiH]^{\bullet+}$, lies about 60 kcal mol^{-1} higher in energy than the most stable open isomer, $^{\bullet}CH_2OSi^+$, which corresponds to the global minimum on the $[H_2, C, O, Si]^{\bullet+}$ potential energy surface.[18] The weak signals at $SiCH_n^+$ for $n = 0$–2 also argue against the presence of significant amounts of the $CH_2SiO^{\bullet+}$ isomer which our calculations show to lie 23.4 kcal mol^{-1} above the global minimum.[18]

The features at *m/z* 44 and 45 corresponding to the loss of CH_2 and $CH^{\bullet}$ speak to the presence of the connectivity CH_2 while the absence of an ion corresponding to the loss of C implies that both hydrogen atoms are connected to C exclusively. The observation of dominant loss of H_2 (rather than H) is consistent with these conclusions. Also, the extent that Si might resemble C in the C analogue $[H_2, C_2, O]^{\bullet+}$, the previously reported CA results[17] for the radical cations of $CH_2{=}C{=}O$ and $HC{\equiv}COH$ suggest that the structures $SiH_2{=}C{=}O$, $CH_2{=}Si{=}O$, $HSi{\equiv}COH$, and $HC{\equiv}SiOH$ can be ruled out on the basis that H_2 rather than H loss was observed to predominate. Taken together, these observations indicate a connectivity for the cation at *m/z* 58 given by the distonic ion $^{\bullet}CH_2OSi^+$. The *m/z* 44 ion would then arise from simple scission of the C–O bond. The appearance of the relatively weaker peak at *m/z* 45 which corresponds to the ion $HOSi^+$ must then be accompanied by a H 1,2-shift in $^{\bullet}CH_2OSi^+$ to produce $HOSi^+$. A H 1,3-shift to produce the higher energy isomer $HSiO^+$ which is more endothermic[10] is less likely. The other relatively strong peaks at *m/z* 28, 29, and 30 are more difficult to assign unequivocally since they may be due to $CO^{\bullet+}$, CHO^+, and $CH_2O^{\bullet+}$ arising from loss of SiH_2, $SiH^{\bullet}$, and Si, respectively, or due to $Si^{\bullet+}$, SiH^+, and $SiH_2^{\bullet+}$ arising from loss of CH_2O, $CHO^{\bullet}$, and CO, respectively, or due to a combination. CA/CA experiments were not helpful in this regard since only the losses of $H^{\bullet}$ and H_2 were observed from *m/z* 29 and 30, respectively.

However, the interpretation of the peaks observed at *m/z* 28, 29 and 30 is facilitated by a knowledge of the energetics of the possible unimolecular decompositions of the cation at *m/z* 58. Energy barriers along the various paths of unimolecular dissociation are not available, but the overall energetics of dissociation are now known, at least for the distonic ion $^{\bullet}CH_2OSi^+$ for which we have a calculated energy.[18] Table I provides a summary of the calculated energies for the various modes of unimolecular dissociation of the distonic ion $^{\bullet}CH_2OSi^+$. They are seen to be in good agreement with values derived from compilations of enthalpies of formation determined experimentally[30,31] when based on the calculated dissociation of the distonic ion into $Si^{\bullet+}$ and formaldehyde. According to theory, the lowest energy dissociation of the distonic ion which does not involve bond redisposition is formation of $Si^{\bullet+}$ and H_2CO which requires only 68 kcal mol^{-1}. If bond redisposition occurs by ion–molecule reaction before these two species separate, then the transfer of H_2 from H_2CO to $Si^{\bullet+}$ (which is exothermic by 19 kcal mol^{-1}) would produce $SiH_2^{\bullet+}$ (*m/z* 30). Also HCO^+ and SiH^+ (both *m/z* 29) may be formed if H^- or $H^{\bullet}$ transfer occurs before separation, but only if an excess of 14.5 (18) and 10 (14) kcal mol^{-1} is available for the dissociation, respectively. (Here the energies based on compiled values for experimental enthalpies of formation[30] are given in parentheses.) Such excess energies must be available since the most endothermic dissociation channel which was observed unequivocally, viz. the formation of $SiO^{\bullet+} + CH_2$, requires an overall energy of 144.5 (132) kcal mol^{-1} if derived from the distonic ion. Curiously, the more exothermic channel to produce SiO and $CH_2^{\bullet+}$ was almost absent from the CA spectrum. In this case, SiH^+ (*m/z* 29) and $SiH_2^{\bullet+}$ (*m/z* 30) may arise from reactions between $SiO^{\bullet+}$ and CH_2 before they separate. These latter reactions are exothermic by 66 (50) and 98 (83) kcal mol^{-1}, respectively. Loss of $SiH^{\bullet}$ and SiH_2 from the distonic ion $^{\bullet}CH_2OSi^+$ to leave CHO^+ and $CO^{\bullet+}$ is less favorable since these channels are more endothermic than formation of SiH^+ and $Si^{\bullet+}$ by loss of $CHO^{\bullet}$ and CH_2O, respectively.

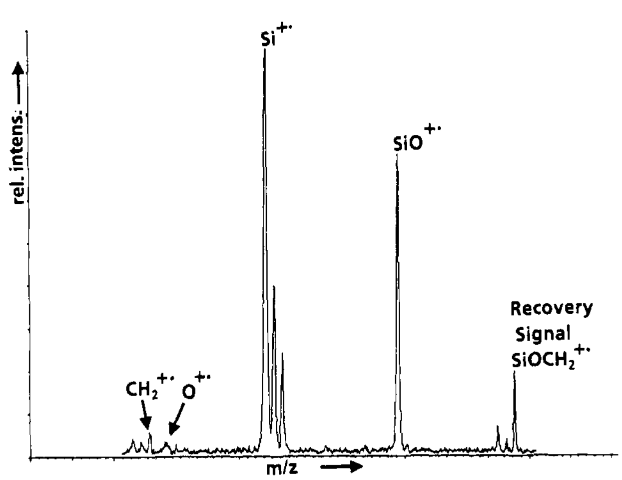

Figure 2. NR mass spectrum (Xe, 70% *T*; O_2, 70% *T*) of $[H_2, C, O, Si]^{\bullet+}$. The total contribution of the isotopic peaks $^{29}SiOCH^+$ and $^{30}SiOC^{\bullet+}$ to the recovery signal of $^{28}SiOCH_2^{\bullet+}$ is 11%.

Figure 2 shows the mass spectrum which is observed when the *m/z* 58 ion is neutralized and reionized in a NRMS-type experiment. The observation of the recovery signal implies the occurrence of nearly vertical neutralization and ionization processes and so a retention of the connectivity and geometry of the initial *m/z* 58 ion. The remainder of the spectrum is supportive of the proposed distonic ion connectivity since it contains the same diagnostic peaks observed in the CA spectrum of the initial *m/z* 58 ion shown in Figure 1 including an amplified signature of the CH_2 linkage in the form of the $C^{\bullet+}$, CH^+, and $CH_2^{\bullet+}$ distribution. The much larger signal of $SiO^{\bullet+}$ at *m/z* 44 relative to $SiOH^+$ at *m/z* 45 may be attributed to contributions from the reionization to $SiO^{\bullet+}$ of SiO and perhaps $SiOH^{\bullet}$ fragments formed in the neutralization step. In addition, the cross-section for $SiOH^{\bullet}$ is smaller than that for SiO.[32] Again, there is no evidence for the

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Table II. Calculated Bond Lengths (Å) for the Distonic Ion $^{\bullet}CH_2OSi^+$ and the Singlet and Triplet States of the Biradical Neutral $^{\bullet}CH_2OSi^{\bullet}$

bond	$^2A'$ (·+)	$^1A'$	$^3A''$
C–O	1.368	1.340	1.328
Si–O	1.574	1.613	1.661

presence of an $SiCH_n$ (n = 0–2) linkage which would be a signature of $OCSiH_2^{\bullet+}$ or $COSiH_2^{\bullet+}$ parent ions.

If the m/z 58 ion is largely the distonic ion $^{\bullet}CH_2OSi^+$, a recovery of the biradical $^{\bullet}CH_2OSi^{\bullet}$, as either a singlet or a triplet, is expected on the basis of our theoretical results which indicate only minor differences in geometry between the distonic ion and the two spin states of the biradical (see Table II).[17] A Franck–Condon transition in the neutralization step could preferentially lead to the singlet biradical which has a geometry closer to that of the distonic ion. A similar suggestion follows from the computed values for the adiabatic and vertical ionization energies for the two spin states of the biradical to yield the distonic ion. Values of IE_v = 6.41 eV and IE_a = 5.75 eV were derived for the triplet, and values of IE_v = 6.71 eV and IE_a = 6.15 eV were derived for the singlet which is slightly more stable. So $IE_v - IE_a$ is 0.66 eV for the ionization of the triplet and only 0.56 eV for the ionization of the single biradical.

Conclusions

1. The results of the collisional-activation and neutralization-reionization experiments together with theory are in keeping with the proposal that the m/z 58 ion derived from $Si(OCH_3)_4^{\bullet+}$ corresponds to the distonic ion $^{\bullet}CH_2OSi^+$.
2. The results of the neutralization-reionization experiments together with theory provide evidence for the stability of the biradical $^{\bullet}CH_2OSi^{\bullet}$ and its formation from the distonic ion $^{\bullet}CH_2OSi^+$ by neutralization at a high collision energy of 8 keV.[33]

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[33] For the generation and characterization of other diradicals from distonic ions in the gas phase, e.g., $^{\bullet}CH_2OCH_2^{\bullet}$, see: Wesdemiotis, C.; Leyh, B.; Fura, A.; McLafferty, F. W. *J. Am. Chem. Soc.* **1990**, *112*, 8655.

Electronic States of Benzo[*a*]pyrene. Linear and Magnetic Circular Dichroism, Polarized Fluorescence, and Quantum Chemical Calculations

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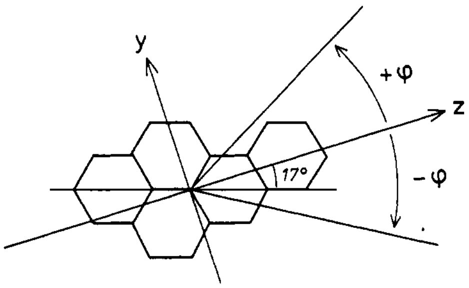
Abstract: The carcinogen benzo[*a*]pyrene is investigated by UV and IR linear dichroism (LD) spectroscopy in stretched polyethylene, by UV magnetic circular dichroism (MCD) spectroscopy, and by fluorescence polarization spectroscopy. The combined results lead to a detailed experimental characterization of transitions in the near-UV region, with determination of polarization directions for five electronic transitions. The experimental results are compared with theoretical predictions using the PPP, CNDO/S, CNDO-SDCI, and LCOAO quantum chemical models. Excellent agreement with observed values in the low-energy region, including transition moment directions and MCD signs, is obtained within the LCOAO model. The theoretical analysis reveals a strong breakdown of the alternant pairing symmetry for benzo[*a*]pyrene, compared with those observed in the related hydrocarbons benz[*a*]anthracene and chrysene.

Introduction

Benzo[*a*]pyrene (BaP), a widespread environmental contaminant and a potent carcinogen, has long been among the most extensively investigated polycyclic benzenoid hydrocarbons.[1] It is thus remarkable that essential features of the electronic structure of BaP remain incompletely elucidated. For example, little seems to be known about the polarization directions of its electronic transitions, although this information is of importance in the study of several aspects of its biological reactivity.[2-4]

In the present investigation we study the electronic spectrum of BaP by experimental and theoretical methods, using a similar approach as in our recent investigations of chrysene[5] and benz[*a*]anthracene[6,7] and a number of derivatives and related com-

Chart I. Benzo[*a*]pyrene (BaP)



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