with the TIPS find a dramatic increase in the gauche–trans ratio for 1,2-dichloroethane in going from the gas phase to the neat liquid.[11] In this instance the more polar gauche conformer (μ = 2.6 D) is preferentially stabilized in polar media in comparison to the trans conformer (μ = 0). However, some folding of *n*-alkanes in water has been predicted[35] and found in Monte Carlo calculations.[36,37] For *n*-butane, the theory of Pratt and Chandler and a simulation both yield a ca. 20% increase in the gauche population upon transfer from the ideal gas phase to aqueous solution.[35,37]

A few comments can be made on the discrepancy between the present findings and those of Bolis et al.[6] All the evidence from their simulations indicates methanol prefers to be eclipsed in water; however, they are aware of the limitations of their computations and say the conformational preference is "an open problem". There are several specific aspects of their study that provide possible sources of error. Again the MCY–CI potential has been employed for the water interactions, and physically unusual boundary conditions were used: the 198 solvent molecules plus the solute were constrained to a sphere with a constant volume commensurate with the density of liquid water. In addition, the water–methanol potential was obtained by fitting to modified ab initio results with a minimal basis set.[6] From Figure 4 in their paper it is apparent that staggered methanol prefers to be a hydrogen bond donor rather than acceptor with water by about 3 kcal/mol. With minimal basis set calculations this difference is normally only ca. 1 kcal/mol and with larger basis sets the preference reverses (Table II).[27] The authors also indicate the eclipsed form is a better hydrogen bond acceptor than the staggered by about 1 kcal/mol. This is surprisingly large for as remote an effect; the present methanol–water potential predicts the conformation of methanol to make less than a 0.1 kcal/mol difference on any hydrogen bond energy. Also, our own experience has been that it is difficult to obtain good intermolecular potential functions for fluid simulations by adding dispersion and other corrections to minimal basis set results.[38] As discussed elsewhere, even high quality ab initio calculations are not necessarily particularly useful in this regard.[39]

In closing this section some final technical details may be noted. There were 862 barrier crossings between different staggered conformers during the final 2000K configurations. Many of the crossings reverted quickly; the number of transitions such that the new well was explored extensively was about 60. The methyl group made several complete circuits, though the tagged hydrogen spent most of its time in the wells for two of the three identical conformers. In this case the umbrella sampling increased the number of barrier crossings by a factor of ca. 2–3. It is apparent that for solutes wih higher rotational barriers umbrella sampling would be very valuable for obtaining adequate sampling of the conformational space.[20]

IV. Conclusion

The present work demonstrates the utility of Monte Carlo simulations in the NPT ensemble with preferential and umbrella sampling for modeling dilute solutions containing organic solutes. This appears to be as efficient an approach as is currently available that includes the solvent molecules explicitly. Many detailed structural insights were obtained for methanol in water. The methyl group is surrounded by a flexible cage of water molecules that blends in to accomodate two to three methanol–water hydrogen bonds. The energies and numbers of hydrogen bonds for the cage molecules are remarkably near normal for bulk water. It was also found that the preferred conformation of methanol in water is staggered as in the gas phase. The reasonable thermodynamic results obtained with the TIPS support the validity of the observations.

Acknowledgment. Gratitude is expressed to the National Science Foundation (CHE80-20466) for support of this study. The authors are also grateful to Professor B. J. Berne for a preprint of ref 36. Dr. J. Chandrasekhar and Professor M. C. R. Symons provided helpful discussions.

Registry No. Methanol, 67-56-1.

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(35) Pratt, L. R.; Chandler, D. *J. Chem. Phys.* **1977**, *67*, 3683.
(36) Rosenberg, R. O.; Mikkilineni, R.; Berne, B. J. *J. Am. Chem. Soc.* **1982**, *104*, 7647.
(37) Jorgensen, W. L. *J. Chem. Phys.* 1982, *77*, 5757.
(38) Jorgensen, W. L. *J. Am. Chem. Soc.* **1980**, *102*, 543.
(39) Jorgensen, W. L. *J. Chem. Phys.* **1981**, *75*, 2026. .

Absorption Spectra and Photochemical Rearrangements of Toluene, Cycloheptatriene, and Norbornadiene Cations to Methylenecyclohexadiene Cation in Solid Argon

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Abstract: Toluene, cycloheptatriene, and norbornadiene cations have been produced and isolated by matrix photoionization methods and their absorption spectra recorded. Absorptions have been identified in agreement with photodissociation and photoelectron spectra. In addition, the photochemistry of these cations has been investigated, showing that they all rearrange into a common methylenecyclohexadiene cation, the McLafferty rearrangement product from gas-phase mass spectrometry studies.

Introduction

The toluene cation and its structural isomers are among the most thoroughly studied cations in mass spectroscopy.[1-5] Of particular interest are the rearrangements among the $C_7H_8^{+\cdot}$ structural isomers that precede decomposition. McLafferty et. al have proposed four rearrangement pathways that account for the observed isotopic scrambling.[3] A common theme from these

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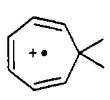
(1) Bursey, J. T.; Bursey, M. M.; Kingston, D. F. I. *Chem. Rev.* **1973**, *73*, 191.
(2) Dunbar, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 472.
(3) Baldwin, M. A.; McLafferty, F. W.; Jerina, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 6169.
(4) Jackson, J.-A. A.; Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1977**, *99*, 7515.
(5) McLafferty, F. W.; Bockhoff, F. M. *J. Am. Chem. Soc.* **1979**, *101*, 1783.

0002-7863/83/1505-1413$01.50/0

studies is that excess internal energy is required for interconversion of $C_7H_8^{+}\cdot$ structural isomers. Since a solid argon matrix cage provides an effective energy sink, the matrix isolation technique was used as a medium to trap $C_7H_8^{+}\cdot$ cations in their different structural forms for observation of their characteristic absorption spectra and to photochemically initiate rearrangements among these different structural isomers without substantial decomposition. A previous matrix photoionization study of cycloheptatriene cation in solid argon produced a broad 480-nm absorption for cycloheptatriene cation (**1**), and irradiation in the latter absorption produced a sharp weak 430.6-nm band that was assigned to the toluene cation.[6] Refinement of the matrix photoionization technique to include CH_2Cl_2 to serve as a dissociative electron-capture trap has increased the yields of cation products that can be matrix-isolated and the subsequent yields of their photochemical rearrangement products. The recent development of a matrix two-photon ionization technique has provided another method for producing and trapping parent cations.[7] We report here new matrix photoionization studies of four C_7H_8 precursors, which give an increased yield of ion products including new broad bands centered at 420 and 276 nm for the toluene cation (**2**), a weak broad band at 650 nm for the norbornadiene cation, and the sharp, strong 430.6-nm band, with a sharp weak 639.4-nm counterpart, which is reassigned to the methylenecyclohexadiene cation (**3**), suggested to explain the exchange between α and ring hydrogen atoms in toluene cations in the gas phase.[3]



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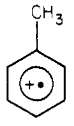

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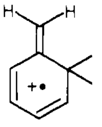

3

Experimental Section

The cryogenic and gas-handling equipment have been described earlier.[6,8] Cations were produced by either direct single photon ionization of precursor molecules with argon resonance vacuum-UV radiation during sample condensation[9] or by a two-photon ionization process involving the illumination of freshly prepared matrix samples by an intense mercury arc lamp (1000 W, Illumination Industries, Inc., BH-6-1).[7] Matrix samples were prepared by condensing toluene (T), cycloheptatriene (C), norbornadiene (N), or quadricyclane (Q) (Aldrich) diluted with argon containing CH_2Cl_2 (argon/CH_2Cl_2/reagent 200–1000:1–5:1) at 2 mmol/h (total gas) with about 1 mmol/h of argon passing through a 3-mm orifice quartz discharge tube onto a 20 K sapphire plate for 2–7 h. Following sample preparation the spectrum between 200 and 800 nm was recorded with a Cary 17 spectrophotometer; then the sample was subjected to a series of glass-filtered mercury arc photolyses and more spectra were recorded. The spectra illustrated here have been digitized using a Nicolet 1180 computer and converted to a wavenumber scale. Band positions are given in the text in units of 10^3 cm^{-1} for simplicity; band positions in the table are given in wavenumber units rounded to the accuracy of ±10 cm^{-1}.

Results

New experiments were performed with toluene, cycloheptatriene, norbornadiene, and quadricyclane using CH_2Cl_2 as an electron trap. These will be described in turn.

Toluene. Two experiments were performed with toluene and CH_2Cl_2 in argon using the matrix two-photon ionization process to produce charged species. Initial spectra recorded after sample condensation but prior to irradiation exhibited no absorption between 6.5 and 50.0 ($\times 10^3$ cm^{-1}) except for toluene precursor absorptions in the UV. Brief illumination (≤ 1 min) of the frozen sample with 220–1000 nm radiation produced two new weak, broad absorptions at 23.8 (full-width at half-maximum = fwhm = 1700 cm^{-1}) and 36.2 (fwhm = 2500 cm^{-1}). Longer photolyses increased the two broad bands and revealed other prominent features near 10.0 (fwhm = 3000 cm^{-1}), 22.3, 23.2, and 32.3.

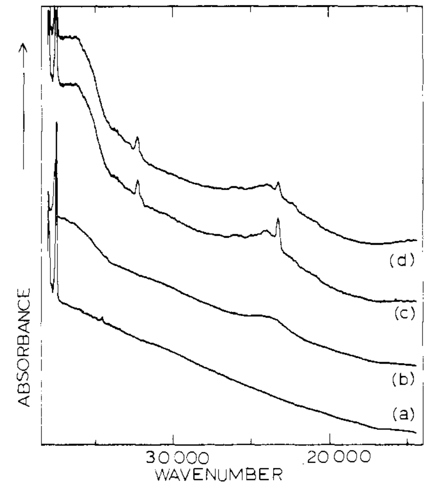

Figure 1. Absorption spectra of Ar/CH_2Cl_2/toluene 1000:2:1 sample at 20 K: (a) spectrum of sample deposited for 4 h, (b) spectrum after 220–1000-nm photolysis for 30 s, (c) spectrum after 220–1000-nm photolysis for 30 min, (d) spectrum after 290–1000-nm photolysis for 30 min.

Figure 1 illustrates selected spectra obtained from the best experiment involving the condensation of an $Ar/CH_2Cl_2/T$ 1000:2:1 sample for 4 h. Trace a shows the spectrum of the condensed sample prior to any irradiation, trace b was obtained after a 30-s 220–1000-nm photolysis, trace c was taken after 30-min irradiation with 220–1000-nm light, and trace d was obtained after 30-min exposure to 290–1000-nm radiation. As noted above, the initial spectrum contains only toluene absorptions, while the spectrum after the first photolysis shows the broad bands at 36.2 (absorbance = A = 0.025) and 23.8 (A = 0.015). Trace c shows that the longer photolysis markedly increased the broad UV and visible bands to A = 0.13 and A = 0.08, respectively, produced sharp bands at 32.3 (A = 0.08), 23.2 (A = 0.09), and 15.6 (A = 0.006) and reduced the first sharp toluene vibronic line at 37 439 cm^{-1} from A = 0.60 to A = 0.52. The sharp 32.3 band due to benzyl radical[10] is the only band produced by mercury arc photolysis of toluene samples in the absence of electron traps. The second photolysis also produced weak broad bands at 22.3 (A = 0.015) and 10.0 (A = 0.02). The 290–1000-nm photolysis, which was unable to efficiently excite toluene, failed to increase the intensity of any of the product absorptions or produce any new absorptions, but it reduced the two sharp bands at 23.2 and 15.6 by about 60%.

The other toluene experiment, using a higher sample concentration ($Ar/CH_2Cl_2/T$ 500:2:1), gave similar photochemical behavior. In this experiment, a longer 220–1000-nm photolysis was performed that reduced the 23.2 and 15.6 bands after bringing them to a maximum; the other absorptions showed no changes. The only noteworthy difference between this experiment and the preceding one was that the intensity for the 10.0- and 22.3-cm^{-1} bands were appreciably larger relative to the other absorptions.

Cycloheptatriene. Five new experiments were performed with cycloheptatriene and CH_2Cl_2 in solid argon. One of these employed the two-photon ionization technique and the others used argon resonance vacuum-UV photoionization methods. The two-photon ionization method failed to give any products while the vacuum-UV method produced a dominant 20.8 absorption that was destroyed by visible photolysis to create other absorptions, some of which were also photosensitive.

Figure 2 shows spectra from one experiment where the photochemistry was studied extensively. Trace a was obtained after $Ar/CH_2Cl_2/C$ 700:2:1 sample was condensed while being exposed to argon resonance radiation for 2.5 h, trace b was obtained after

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(6) Andrews, L.; Keelan, B. W. *J. Am. Chem. Soc.* **1980**, *102*, 5732.

(7) Kelsall, B. J.; Andrews, L. *J. Chem. Phys.* **1982**, *76*, 5005.

(8) Andrews, L. *J. Chem. Phys.* **1975**, *63*, 4465.

(9) Andrews, L.; Tevault, D. E.; Smardzewski, R. R. *Appl. Spectrosc.* **1978**, *32*, 157.

(10) Andrews, L.; Miller, J. H.; Keelan, B. W. *Chem. Phys. Lett.* **1980**, *71*, 207.

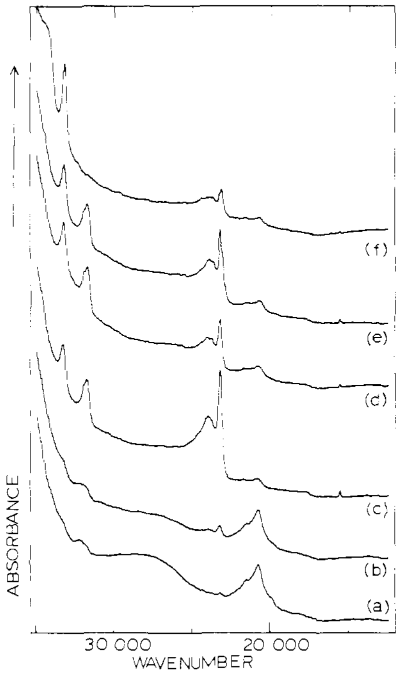

Figure 2. Absorption spectra of Ar/CH_2Cl_2/cycloheptatriene 700:2:1 sample at 20 K: (a) spectrum of sample deposited for 2.5 h with concurrent vacuum-UV photoionization, (b) spectrum after 500–1000-nm photolysis for 5 min, (c) spectrum after 470–1000-nm photolysis for 3 h, (d) spectrum after 370–460-nm photolysis for 30 min, (e) spectrum after 470–1000-nm photolysis for 30 additional min, (f) spectrum after 290–420-nm photolysis for 1 h.

a 5 min exposure to 500–1000-nm radiation, trace c represents the spectrum after 3-h irradiation with 470–1000-nm light, trace d shows the spectrum following a 30-min photolysis with 370–460-nm radiation, trace e shows the spectrum after an additional 30-min exposure to 470–1000-nm light, and trace f was taken following a 1-h illumination with 290–400-nm radiation. The spectrum of the freshly prepared sample exhibits a dominant absorption at 20.8 (A = 0.12) with shoulders at 19.9, 21.6, and 22.3, a sharp weak band at 23.2 (A = 0.008), a weak poorly resolved doublet at 31.8 and 32.0 (A = 0.009), and a weak shoulder at 33.2 on the sample background. The very broad absorption at 27.2 due to the $CH_2Cl_2^+$ molecular cation,[11] was always observed in argon resonance photoionization experiments with CH_2Cl_2. The 500–1000-nm photolysis completely destroyed the $CH_2Cl_2^+$ absorption, reduced the 19.9 band by 50% and the 20.8, 21.6, and 22.3 series of bands by 20%, while it increased the 23.2 band (Figure 2b). Prolonged photolysis with more energetic 470–1000-nm radiation completely destroyed the 19.9 band and reduced the 20.8, 21.6, and 22.3 group of bands to 20% of their original intensity; at the same time the 23.2 peak increased to A = 0.31, revealing poorly resolved structure at 23.8 and 24.0 and a very sharp band at 15.6 (A = 0.025) (Figure 2c). In addition, the bands in the UV region at 31.8 (A = 0.12), 32.0 (A = 0.08), and 33.2 (A = 0.13) increased substantially. Photolysis in the 23.2, 23.8, and 24.0 group of absorptions with 370–460-nm radiation reduced this group and the 15.6 band by half, increased the 20.8 group by 50%, and did not change the UV spectral features (Figure 2d). A second photolysis with 470–1000-nm light slightly reduced the 20.8, 21.6, and 22.3 group, increased the UV bands, and partially restored the 23.2, 23.8, 24.0, and 15.6 absorptions. The 370–460-nm photolysis followed by a 470–1000-nm photolysis cycle was repeated several times with each successive one promoting a smaller change. The final photolysis at 290–420 nm reduced all of the visible absorptions, destroyed the 31.8–32.0 doublet, revealing a weak 32.3 band, increased the 33.2 absorption, and produced a new broad band at 34.2 (A = 0.09) (Figure 2f).

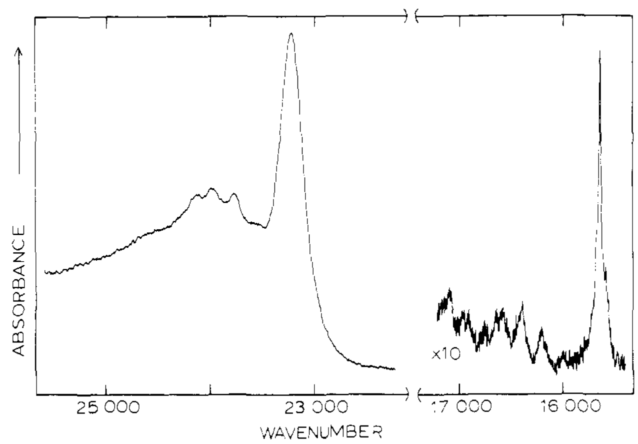

Figure 3. Expanded scale spectrum of the 15 640- and 23 220-cm^{-1} band systems assigned here to methylenecyclohexadiene cation in solid argon.

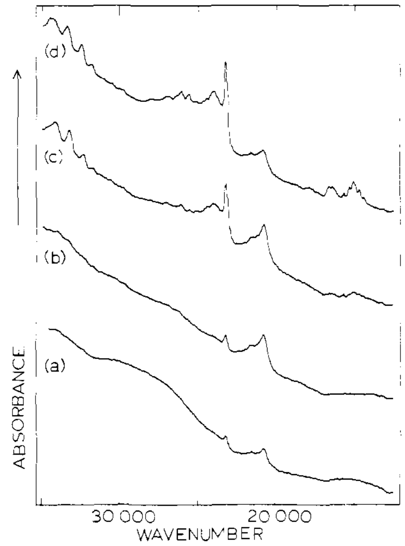

Figure 4. Absorption spectra of Ar/CH_2Cl_2/norbornadiene 400:1:1 sample at 20 K: (a) spectrum after deposition for 4.5 h with simultaneous vacuum-UV photoionization, (b) spectrum after 500–1000-nm photolysis for 10 min, (c) spectrum after 240–420-nm photolysis for 10 min, (d) spectrum after 470–1000-nm photolysis for 2 h.

The other cycloheptatriene experiments were performed to search for other weak absorptions which could be associated with the principal product absorptions. After longer 7-h sample preparation, the same bands were produced with increased intensity (20.8, A = 0.33), and a weak new absorption appeared between 12.8 and 15.9 with partially resolved structure peaking at 13.9 (A = 0.012); a careful examination of the spectra between 6.6 and 12.5 showed no product absorptions. The 13.9 band was about 3% of the intensity of the 20.8 band, and it exhibited similar photochemical behavior. After 240–420- and 470–1000-nm photolysis, the 15.6 absorption (A = 0.03) appeared in the spectrum along with weak new bands at 16.2, 16.4, and 16.7 (A = 0.005). Figure 3 illustrates the 15.6 and 23.2 band origins and their associated vibronic structure.

Norbornadiene. Three experiments were performed using norbornadiene as a precursor; two used the argon resonance photoionization method and the other used the mercury arc as a two-photon ionization source. The latter yielded no product bands while the first two gave a series of weak bands that underwent substantial photoinduced changes.

Spectra from one of the argon resonance experiments are illustrated in Figure 4. Trace a represents the spectrum of the freshly prepared matrix after a 4.5-h deposition, trace b was taken after a 10-min exposure to 500–1000-nm radiation, trace c followed 10-min irradiation with 240–420-nm photons, and trace d was obtained after a 2-h 470–1000-nm photolysis. The initial

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[11] Andrews, L.; Prochaska, F. T.; Ault, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 9.

spectrum shows a broad weak band at 15.4 (A = 0.008, fwhm = 3000 cm^{-1}) and sharper weak bands at 20.8 (A = 0.03), 21.6, and 23.2 (A = 0.02) which were observed in the earlier cycloheptatriene studies; again, the broad band at 27.2 is due to $CH_2Cl_2^+$. The 500–1000-nm photolysis substantially decreased the broad 15.4 absorption, substantially increased the 20.8 (A = 0.06) and 21.6 bands, and slightly increased the 23.2 band. The subsequent photolysis in only the UV region had virtually no effect on the 20.8 and 21.6 bands, but it substantially increased the 23.2 (A = 0.12) band and associated structure at 23.8 and 24.0. In addition the UV photolysis produced a series of bands at 31.7, 32.3 33.2, and 34.2, a series of weaker bands in the blue region of the spectrum at 24.5, 25.6, 26.1, 26.9, and 27.1, and another series of poorly resolved bands in the red spectral region at 14.4, 14.7, 14.9, 15.0, 15.3, 16.2, 16.4, and 16.6, and a sharp 15.6 (A = 0.008) absorption. Prolonged irradiation at 470–1000 nm substantially reduced the 20.8 and 21.6 bands, left the UV series unchanged, and increased all other product bands by about 50%.

Quadricyclane. Two argon resonance photoionization experiments were performed with quadricyclane using CH_2Cl_2 as an electron trap. The results with this precursor were nearly the same as with the norbornadiene. The initial spectra following sample condensation showed a slighly smaller yield of the broad 15.4 band and the 20.8, 21.6, and 23.2 bands with no evidence of any other products due to the precursor. A 500–1000-nm photolysis of the initial sample in one experiment slightly increased the 23.2 band and significantly increased the 20.8 and 21.6 bands, whereas in the other experiments a 240–420-nm photolysis produced all of the bands detected in the norbornadiene experiments. Subsequent photolyses in both experiments using 220–1000-nm radiation increased the three series of bands in the red, blue, and UV spectral regions and markedly reduced the 20.8 and 21.6 bands as well as the sharp 15.6 and 23.2 bands and their associated structure. The experiments with Q produced relatively stronger red series bands and weaker blue series bands than the N precursor.

Discussion

The absorptions will be identified first and then the important photochemistry of the $C_7H_8^+$ cation system will be discussed.

Identification. The broad 23.8 and 36.2 absorptions produced by mercury arc photolysis of toluene in frozen argon, which were markedly enhanced by the presence of good electron trapping molecules, are assigned to the toluene radical cation. The positions and shapes of these absorptions are in excellent agreement with the ICR photodissociation bands[12] of gaseous toluene cation at 24.0 and 37.4, although the matrix absorption spectrum (MAS) bands are red-shifted 200 and 1200 cm^{-1}, respectively, owing to interaction with the argon matrix. The higher excited state interacts more strongly with the matrix as the electron affinity of the excited state approaches the ionization energy of argon. The MAS bandwidths are about half of the photodissociation bandwidths[12] owing to efficient internal energy quenching by the frozen argon medium. The 23.8 band can be attributed to the promotion of an electron in the lowest energy π level to the partially filled highest occupied level (benzene a_{2u}–b_{1g}) in agreement with the difference between the first and third photoelectron bands for toluene.[13] The 36.2 band is due to the promotion of the single electron in the highest occupied π level to the lowest unoccupied π^* level (benzene $e_{1g} \rightarrow e_{2u}$). Although a direct comparison with the neutral molecule is impossible for the first transition, the π–π^* transition shows a 3000-cm^{-1} red shift as measured for the onset of the cation absorption and the peak of the vibronic origin for the neutral molecule. Careful examination of the MAS showed evidence of another cation absorption beginning near 44.5 which became masked by the very strong ^1B_u parent absorption before it reached a maximum. This cation absorption probably corresponds to the neutral transition that obscures most of the former.

The 20.8, 21.6, and 22.3 bands are assigned to the cycloheptatriene radical cation. In an earlier matrix study,[6] the 20.8, 21.6, and 22.3 bands were assigned to cycloheptatriene cation along with several other lower energy absorptions. The present study using electron-trapping techniques that prevent unwanted ion destruction by photobleaching shows that the lower energy bands belong to other species which will be discussed below, and that the 750-cm^{-1} vibronic progression begins at 20.8. The 20.8 band origin agrees very well with the cycloheptatriene cation peak in ICR photodissociation studies at 21.3, with the 21.5 difference between the first and third photoelectron bands, and with the strong 20.7 peak in an irradiated cycloheptatriene–Freon mixture glass.[14-16] Although the photoelectron data suggest an assignment of the 20.8 band to the excitation of an electron in the lowest π orbital to the partially filled highest occupied π molecular orbital, experiments and calculations on different hexatriene configurations indicate that a cyclic conjugated triene cation should have a transition in this region with significant π to π^* character.[16] The data collected here are insufficient to identify the upper state of the transition.

The region from 17.0 to 7.0 was searched for the weak red absorption expected for cycloheptatriene cation. The only candidate was the weak structured band peaking at 13.9, which exhibited the same general photochemical behavior as the 20.8 band, as far as could be determined for a weak, broad band. The 13.9 argon matrix band is in agreement with a similar 13.7 band produced by irradiation of cycloheptatriene in a Freon matrix.[16] Although the first and second bands in the photoelectron spectrum predict a red absorption near 9.8, the fact that cycloheptatriene is not planar suggests that the radical cation may undergo considerable structural relaxation owing to hyperconjugation with the CH_2 group. The broad Franck–Condon profile of the weak 13.9 band is consistent with this hypothesis. The position of the 13.9 band is only slightly red-shifted from the lowest energy transition for the hexatriene radical cations. Additional support for this possible assignment to cycloheptatriene cation comes from theoretical calculations, which show that the lowest energy transition, predominantly $\pi_2 \rightarrow \pi_3$ character, is shifted the most to the red with cyclic configurations.[16]

The broad 15.4 band detected in both the norbornadiene and the quadricyclane experiments is assigned to the norbornadiene radical cation. Support for this assignment comes from the larger yield of the 15.4 band in the norbornadiene experiments compared with the quadricyclane experiments, and from thermochemical estimates, which suggest that norbornadiene cation is more stable than quadricyclane cation at 77 K. Similar results were obtained in γ-radiolysis studies of norbornadiene and quadricyclane in hydrocarbon glasses at 77 K, which produced a very broad 15.7 band for both precursors.[17] MINDO/3 calculations show three low-energy $\pi \rightarrow \pi$ transitions; the lowest energy one between the completely filled a_1 level to the half-filled b_2 level is predicted at 6.8, outside the spectral region surveyed. The next transition between the half-filled b_2 level to the lowest unoccupied level, b_1, is electric dipole forbidden. The third transition, from the a_1 level to the b_1 level, is predicted to occur at 14.7 and represents the most probable assignment for the 15.4 band.[17]

Absorptions at 10.0 and 23.3 assigned to the toluene dimer cation compare favorably with 10.8 and 21.5 assignments to toluene dimer cation in glassy matrices at 77 K.[18] Similar benzene dimer cation bands have been observed at 11.1 and 22.1 in matrix photoionization studies.[19] The relative enhancement of the dimer yield with increasing concentration supports an aggregate assignment. The benzene analogue indicates that the 10.0 band is

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(12) Teng, H. H.; Dunbar, R. C. *J. Chem. Phys.* **1978**, *68*, 3133.

(13) Baker, A. D.; May, D. P.; Turner, D. W. *J. Chem. Soc. B* **1968**, 22.

(14) Dunbar, R. C.; Fu, E. W. *J. Am. Chem. Soc.* **1973**, *95*, 2716.

(15) Bodor, N.; Dewar, M. J. S.; Worley, S. D. *J. Am. Chem. Soc.* **1970**, *92*, 19. The PES of cycloheptatriene sent to us by E. Heilbronner shows the onset of ionization at 8.30 eV (8.57 eV vertical), a second band peaks at 9.52 eV, and the third band peaks at 10.96 eV. This predicts an absorption maximum for the cation at 21 500 cm^{-1}.

(16) Shida, T.; Kato, T.; Nosaka, Y. *J. Phys. Chem.* **1977**, *81*, 1095. Shida, T., unpublished results.

(17) Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* **1979**, *62*, 583.

(18) Badger, B.; Brocklehurst, B. *Trans Faraday Soc.* **1969**, *65*, 2582.

(19) Miller, J. H.; Andrews, L.; Lund, P. A.; Schatz, P. N. *J. Chem. Phys.*, **1980**, *73*, 4932.

a charge-transfer transition between the two rings and that the 22.3 band corresponds to the $\pi \rightarrow \pi$ transition observed at 23.8 for the toluene radical cation.

The sharp band origin absorptions at 23.2 and 15.6 are assigned to the 5-methylenecyclohexadiene radical cation. The 23.2 band was assigned earlier to the toluene cation owing to its presence in the region where toluene cation absorbs and its photosynthesis from cycloheptatriene cation.[6] The present study using dissociative capture electron traps ($CH_2Cl_2 + e \rightarrow CH_2Cl + Cl^-$), which do not detach electrons with visible light, allowed for higher yields of the 23.2 band carrier to be trapped, thus revealing the much weaker important diagnostic 15.6 band, which cannot be due to toluene radical cation. As can been seen in Figures 1 and 2, the 15.6 band increased and decreased with the 23.2 band on photolysis. The two bands were observed with the same relative intensity from the toluene, cycloheptatriene, norbornadiene, quadricyclane, and 1-phenyl-2-butene precursors (see below) which confirms their assignment to the same species. Appearance of the 23.2 band between the 26.4 band of trans–trans–trans hexatriene radical cation[16] and the 20.8 band for the cis–cis–cis cycloheptatriene radical cation and the appearance of the 15.6 band near the weak 15.5 hexatriene cation band indicates a conjugated triene cation with some cyclic character. The instability of the trans–cis–cis hexatriene[16] conformer due to the repulsions between the hydrogens on C(2) and C(6) is removed in the cyclic **3** configuration. The existence of single sharp bands for the 23.2 and 15.6 band origins requires a single geometric structure with no cis–trans isomerization like that found for hexatriene cations in a recent matrix isolation study.[20] The above spectroscopic evidence and the mechanistic arguments to follow conclusively show that the 23.2 and 15.6 bands are due to the methylenecyclohexadiene cation, **3**. Specific assignment of the transitions follows those made for the hexatriene[16] and cycloheptatriene radical cations, the 23.2 band belonging to $\pi \rightarrow \pi^*$ transition involving the highest occupied level and the lowest unoccupied level or a $\pi \rightarrow \pi$ type involving the lowest occupied level and the partially vacant highest occupied level; the 15.6 band belongs to $\pi \rightarrow \pi$ type involving predominantly the partially filled highest occupied level and the next lower fully occupied level. The common vibrational fine structure of 550 and 770 cm^{-1} for the 23.2 band and that of 560 and 750 cm^{-1} for the 15.6 absorption are reasonable for skeletal deformation and single-bond stretching motions of a cyclic diene. These intervals compare favorably with similar vibrations of 1,3-cyclohexadiene observed in the Raman spectrum.[21]

The strong 23.2 argon matrix band is in very good agreement with the strong 24.0 band in the ICR photodissociation spectrum[22] of a $C_7H_8^{+\cdot}$ species produced by the McLafferty rearrangement[23] of *n*-butylbenzene cation and identified as **3**. The 23.2 band was observed in the previous matrix photoionization experiments with *n*-butylbenzene,[6] and the yield increased in subsequent experiments with the addition of CH_2Cl_2. Agreement of the sharp 15.6 argon matrix band with the weaker 17.5 band in the photodissociation spectrum is less satisfactory, which may be due to the fact that the sharp matrix band is a vibronic origin and the broad photodissociation band is broadened over excited vibrational levels because of the presence of excess internal energy. A similar difference between sharp matrix band origins and broad photodissociation bands has been noted for naphthalene cation.[24] This difference between the gaseous and matrix-isolated cations is reinforced by a comparison of the broad 24.0 photodissociation band (fwhm = 5000 cm^{-1}) and the sharp 23.2 argon matrix band (fwhm = 200 cm^{-1}).

The weak photosensitive absorption at 19.9 is tentatively assigned to the norcaradiene cation. Because of its highly strained nature, the norcaradiene cation is expected to be very reactive. As will be discussed below, the norcaradiene cation is probably the intermediate **1** passing through to form **3**. In another matrix photoionization study using benzocycloheptatriene as a precursor,[25] the benzonorcaradiene cation was formed and trapped as an intermediate in solid argon. The effect of the benzo substituent is to render the norcaradiene cation more stable and to shift its absorption spectrum to lower energy.

The 25.6, 26.1, and 26.9 absorptions observed only with bicyclic precursors are tentatively assigned to a substituted hexadiene–yne cation formed by complete ring opening of the bicyclic cation. These bands are very close to the strongest hexatriene radical-cation absorptions.[16,20] The similar bands between 14.4 and 16.6 were favored in Q experiments. Since Q readily undergoes cycloadditions to olefins to give polycyclic systems,[26] a parent dimer may be involved here, and the 14.6–16.6 bands are tentatively assigned to higher order conjugated polyene cations. The position of these bands is to lower energy than the most intense bands for the octatetraene cation,[20] suggesting a still higher order polyene cation. The presence of such a large number of bands with no single one representing an obvious electronic origin suggests a number of structural isomers with similar electronic transitions.

The absorptions at 31.8, 32.3, 33.2, and 34.2 were photoproducts in C, N, and Q experiments with varying relative intensities between the cyclic and bicyclic precursors. Similar bands were produced in methyl- and ethylcycloheptatriene experiments; the band positions are dependent on the alkyl substituent but not the position of the substituent. The two dominant UV bands in the C experiments were produced at the expense of **1** on 470-nm photolysis (Figure 2), which suggests $C_7H_7^+$ daughter cations, a possibility also suggested by the absorption positions intermediate between benzyl cation at 28.3 and tropylium cation at 38.0 in solid argon.[27] Since the tropylium cation is expected to be the major dissociation product of **1**, its subsequent photochemical rearrangement products might contribute to the spectrum. The norbornadienyl cation has been produced by rearrangement of tropylium cation, and a bicyclo[3.2.0]heptadienyl cation intermediate has been implicated.[28] Second daughter $C_5H_5^+$ cations can also be produced[29] from $C_7H_7^+$ with the UV irradiation used here so possible cation products of this formula must also be considered.

Table I summarizes all of the product bands giving absorption energies in cm^{-1}, assignments, and precursors.

Photochemistry. The cycloheptatriene and norbornadiene radical cations are formed directly from the appropriate precursor by the 11.6–11.8-eV argon resonance lamp. The cations formed by the method are probably formed with excess internal energy since the energy of the argon resonance radiation is considerably higher than the first ionization energies of 8.3 and 8.4 eV for cycloheptatriene and norbornadiene, respectively.[15,17] Most of this excess energy is quenched by the solid argon host to give the ground-state cation; however, some excited cations may rearrange to other structures during the condensation and quenching process. Quadricyclane, which has a 7.9-eV ionization energy, is apparently an extreme case because its cation rearranges into the norbornadiene cation before significant quenching can occur.

In the present study, toluene and toluene dimer cations were formed by a two-photon ionization mechanism which efficiently excites the neutral molecule to a higher state that can absorb a second low-energy photon in a high cross-section process to cause photoionization.[7,30] The advantage of this method is that it can produce some cations very efficiently with less destructive radiation. The failure to detect toluene cation in the earlier photoionization work is probably due to more rapid rearrangement

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(20) Kelsall, B. J.; Andrews, L., to be published.

(21) DiLauro, C.; Neto, N.; Califano, S. *J. Mol. Struct.* **1969**, *3*, 219.

(22) Dunbar, R. C.; Klein, R. *J. Am. Chem. Soc.* **1977**, *99* 3744.

(23) Levsen, K.; McLafferty, F. W.; Jerina, D. M. *J. Am. Chem. Soc.* **1973**, *95*, 6332.

(24) Andrews, L.; Kelsall, B. J.; Blankenship, T. A. *J. Phys. Chem.* **1982**, *86*, 2916.

(25) Kelsall, B. J.; Andrews, L., to be submitted for publication.

(26) Haselback, E.; Martin, H. D. *Helv. Chim. Acta* **1974**, *57*, 472.

(27) Andrews, L.; Keelan, B. W. *J. Am. Chem. Soc.* **1981**, *103*, 99.

(28) Hogeveen, H.; Gaasbeek, C. J. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 1079.

(29) McCrery, D. A.; Freiser, B. A. *J. Am.* Chem. *Soc.* **1978**, *10*, 2902.

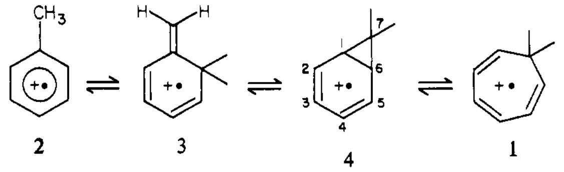
(30) Duncan, M. A.; Dietz, T. G.; Smalley, R. E. *J. Chem. Phys.* **1981**, *75*, 2118.

Table I. Band Positions and Assignments for Species Produced in Matrix Photoionization Studies of Toluene, Cycloheptatriene, Norbornadiene and Quadricyclane

assignments	cm^{-1}	precursor[a]
toluene$^{+\cdot}$ (**2**)	23 800	T
	36 200	T
(toluene)$_2^{+\cdot}$	9 950	T
	22 300	T
cycloheptatriene$^{+\cdot}$ (**1**)	(13 840)	C
	20 800	C, N, Q
	760[c]	C, N, Q
	1 520	C
norbornadiene$^{+\cdot}$ (**4**)	15 400	N, Q
5-methylenecyclohexadiene$^{+\cdot}$ (**3**)	15 640	T, C, N, Q, P
	560[c]	C
	750	C
	1 110	C
	23 220	T, C, N, Q, P, B
	550[c]	T, C, N, Q, P
	770	T, C, N, Q, P
	900	T, C
	1 430	C
(norcaradiene$^{+\cdot}$)[b]	19 940	C
(daughter cations)	31 770	C, N, Q
	32 010	C
	32 320	C, N, Q
	33 250	C, N, Q
	34 170	C, N, Q
(hexadiene-yne$^{+\cdot}$)	25 620	N, Q
	26 110	N, Q
	26 860	N, Q
(polyenes$^{+\cdot}$)	14 380	N, Q
	14 660	N, Q
	14 930	N, Q
	15 040	N, Q
	15 300	N, Q
	16 240	N, Q
	16 390	N, Q
	16 630	N, Q

[a] Precursor identifications: toluene (T), cycloheptatriene (C), norbornadiene (N), quadricyclane (Q), 1-phenyl-2-butene (P), *n*-butylbenzene (B). [b] Parentheses denote tentative assignments. [c] Vibrational intervals (cm^{-1}) from origin band.

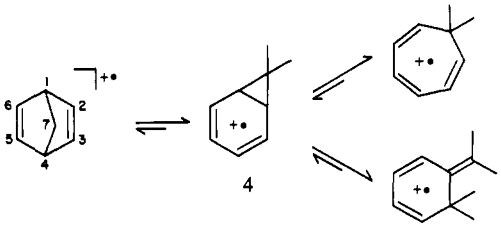
Scheme I



of the excited-state cation than relaxation to the ground-state cation.

The methylenecyclohexadiene cation, **3**, was formed by rearrangement of both cycloheptatriene and toluene cation precursors. In the toluene photolysis experiments, toluene cation, **2**, was produced first, and then the methylenecyclohexadiene cation, **3**, was formed without involving any detected intermediates, while the cycloheptatriene experiments suggest that the methylenecyclohexadiene cation was formed from the cycloheptatriene cation possibly through the norcaradiene cation intermediate, **4**. Scheme I illustrates these two pathways. The methylenecyclohexadiene cation can be formed readily from toluene cation by a 1,3-hydrogen shift that is initiated by light absorption. Examination of the structures in Scheme I and the rearrangement mechanism of McLafferty et al.[3] shows that cycloheptatriene cation cannot readily form methylenecyclohexadiene cation without passing through the norcaradiene cation intermediate. Here, cycloheptatriene cation must be excited into a state which favors ring contraction to form the highly unstable norcaradiene cation intermediate. Once formed, the norcaradiene cation can undergo several rearrangements involving the rupture of the cyclopropane ring. The easiest rearrangement breaks the C(1)–C(6) bond and gives back the cycloheptatriene cation precursors while more difficult rearrangements involve C(7)–C(1) bond rupture and a 1,2-hydrogen shift to give either toluene cation or the methylenecyclohexadiene cation.

Scheme II



The spectra in Figures 2c and 2d show that the **1** ⇄ **3** cation rearrangement is a reversible process although the **1** → **3** direction is favored in these experiments. This dynamic rearrangement is initiated by irradiation into the absorption band of one structure, which provides the required activation energy; the other structure formed in the rearrangement process is deactivated and trapped by the cold matrix. The photochemical stability found for **3** in these experiments suggests that **3** may be an important intermediate in gaseous $C_7H_8^{+\cdot}$ cation rearrangements.

The methylenecyclohexadiene cation was also formed from *n*-butylbenzene in matrix photoinonization experiments involving the McLafferty rearrangement mechanism.[22,23] The **3** cation was, however, produced in greater yield from the analogous rearrangement of 1-phenyl-2-butene cation in similar matrix photoionization studies;[31] the 23.2 band yield was sufficiently great in the latter experiments to observe the weaker 15.6 band.

The rearrangement of the norbornadiene cation may also proceed through the norcaradiene intermediate. The observation that photoisomerization of the norbornadiene cation to cycloheptatriene cation proceeds very rapidly with low-energy visible light suggest a simple rearrangement process involving C(7)–C(4) bond rupture and C(7)–C(2) bond formation, as outlined in Scheme II. The fact that the methylene cyclohexadiene cation absorption grew slightly during the low-energy photolysis also supports a norcaradiene mechanism. Furthermore, the relatively low yield of methylenecyclohexadiene shows that norcaradiene cation preferentially opens to give cycloheptatriene cation even though the methylenecyclohexadiene cation may be more stable.

The polyene cations were produced only in the norbornadiene and quadricyclane experiments, which shows that they are not produced through a norcaradiene intermediate. It is unlikely that they are formed from the parent cation since these bands were not detected until after the parent cation was destroyed. The most probable mechanism for their formation involves rearranged Diels–Alder dimer cation adducts. Such adducts would be required to form conjugated higher polyene cations from $C_7H_8^{+\cdot}$ precursors.

Conclusions

Matrix two-photon ionization of toluene samples first produced broad 23.8 and 36.2 bands in agreement with photodissociation bands for toluene cation and then produced sharp weak 15.6 and strong 23.2 bands. Photoionization of cycloheptatriene during condensation gave a strong 20.8 band for the parent cation in agreement with photoelectron band differences; photolysis in the 20.8 band produced the sharp 15.6 and 23.2 bands. Similar experiments with norbornadiene gave a broad 15.4 band for this parent cation; photolysis in the 15.4 band gave the same 20.8, 15.6, and 23.2 bands. The sharp weak 15.6 and strong 23.2 bands are characteristic of a conjugated triene cation. Coupled with mechanistic evidence from a considerable number of mass spectroscopic investigations, the 15.6 and 23.2 bands are assigned to the 5-methylenecyclohexadiene cation. The formation of methylenecyclohexadiene cation by photochemical rearrangement

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(31) Andrews, L.; Kelsall, B. J.; Harvey, J. A.; Duffy, D. C. *J. Am. Chem. Soc.* **1981**, *103*, 6415.

of toluene, cycloheptatriene, and norbornadiene cations in these matrix experiments suggests that the former may be an important intermediate in gaseous $C_7H_8{}^{+\cdot}$ cation rearrangements. The argon matrix is an effective medium for the investigation of photochemical rearrangement processes in molecular cations.

Acknowledgment. The authors gratefully acknowledge financial support from National Science Foundation Grant CHE 79-10966, helpful discussions with D.S. Kelsall, and a copy of the unpublished spectrum of cycloheptatriene cation in a Freon matrix from T. Shida.

Registry No. 1, 34488-67-0; **2**, 34504-47-7; **3**, 83242-01-7; **4**, 84559-58-0; quadricyclane, 278-06-8; toluene, 108-88-3; 1,3,5-cycloheptatriene, 544-25-2; 2,5-norbornadiene, 121-46-0; toluene dimer cation radical, 59647-14-2; 2,5-norbornadiene cation radical, 41153-22-4.

La Coupe du Roi and Its Relevance to Stereochemistry. Combination of Two Homochiral Molecules To Give an Achiral Product

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Abstract: The problem of dividing finite geometric objects into isometric segments is examined, including the special case in which an achiral object is bisected into isometric homochiral halves (la coupe du roi). Segmentations that are applicable to molecular systems are shown to be limited to four classes, depending on whether or not the object (molecular model) is achiral, whether or not the combination of the cut and the object (cut–object) is achiral, and whether or not there are mirror elements that pass through the segments. These segmentations have a bearing on previously developed relationships among atoms or groups of atoms in molecules and on chemical fragmentations and combinations of molecules. A chemical analogue for the assembly of two homochiral objects into one achiral object (the reverse of la coupe du roi) is provided by the self-coupling of (+)-4-(bromomethyl)-6-(mercaptomethyl)[2.2]metacyclophane ((+)-**15**) to give, in a stereospecific manner, the achiral cis dimer **11** (C_{2v} symmetry). In contradistinction, self-coupling of racemic **15** gives a 1:1 mixture of the above cis dimer and of the trans dimer **12** (C_{2h}): corresponding segments that are homochiral in **11** are heterochiral in **12**.

Consider an apple as an achiral object with the stem at the top (Figure 1). Two vertical half-cuts are made through the apple, one from the top to the equator and the other, perpendicular to the first, from the bottom to the equator. Two nonadjacent, horizontal quarter-cuts are then made along the equator to connect the vertical cuts, and the apple separates into two halves (Figure 1). This parlor trick, known among some families in France as la coupe du roi, is remarkable in that the two halves are homochiral.[2,3] At a first glance, the two halves, which are obviously chiral, might be thought to be mirror images of one another, since together they constitute an achiral object. Not only is this not the case, but it is actually impossible to cut an apple in this way, i.e., into two heterochiral[3] parts. Of course, it is possible to cut an apple in a coupe-du-roi manner in two different but mirror-image related ways, depending on the direction of the quarter-cuts. Such mirror-image related halves, obtained from two different apples, do not however mesh properly to reconstitute an object that looks like a single complete apple (Figure 1). This property is obviously shared by geometric objects such as right circular cones ($C_{\infty v}$) in general, and by right circular cylinders ($D_{\infty h}$) and spheres (K_h) for bisections. However, a moment's reflection reveals that there exists another class of objects in which bisection cannot result in homochiral halves, as exemplified by a triangular pyramid with C_s symmetry or a distorted cube with C_i symmetry.

These considerations piqued our curiosity and provided the impetus for the present work. In this paper we examine the general problem of dissecting finite objects into isometric[3] segments, including the special case of la coupe du roi, and show that this and other segment compositions bear a significant relationship to chemical structures and processes. Finally, we provide a chemical example of such a process.

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(1) (a) University of California, Los Angeles. (b) Princeton University.

(2) (a) Martin Gardner has given a description of this "curious way of dividing an apple into two identical parts" [Gardner, M. "Encyclopedia of Impromptu Magic"; Magic: Chicago, 1978; pp 7 and 8]. Gardner has also pointed out [Gardner, M. *Sci. Am.* **1978**, *239* (5), 22] that this division performed on a sphere has been set in stone by the Swiss artist Max Bill in his granite sculpture "Half Sphere around Two Axes". He additionally notes that this shape "suggests a three-dimensional version of the yin-yang bisection of a circle into asymmetric, congruent parts". (b) The homochiral relationship between the two halves was discovered in 1937 by Alain Horeau, then working in the laboratory of Marcel Delépine (Horeau, A., private communication).

(3) Because our exposition requires the use of stereochemical terminology that may be unfamiliar to the general reader, a brief glossary is provided. Two objects are *isometric*[4a] if they are properly (directly) or improperly (oppositely) congruent; otherwise they are *anisometric*. This definition is applicable to the model of a molecule.[4b] Alternativley phrased,[4c] nuclear configurations are isometric if their labeled graphs are the same, the labeling being by nuclear charge and mass for the vertices and by internuclear distances for the edges. The terms[4d] *homochiral* and *heterochiral* as used in this text refer to relations between isometric chiral objects or models of chiral molecules: homochiral objects are only properly congruent, whereas heterochiral (enantiomorphous) objects are only improperly congruent (isometric achiral objects are both). In the context of the present discussion, there is no need to place an additional restriction on the meaning of these terms.[4e] All of the above terminology may be extended to portions of objects or of models of molecules. If such portions are related by a symmetry operation of the ensemble, they are *homotopic* or *enantiotopic*, depending on whether the symmetry operation is of the first or only of the second kind, respectively.

(4) (a) For an excellent discussion of the concept of isometry, see: Coxeter, H. S. M. "Introduction to Geometry", 2nd ed.; Wiley: New York, 1969. (b) Mislow, K. *Bull. Soc. Chim. Belg.* **1977**, *86*, 595. (c) Bauder, A.; Meyer, R.; Günthard, Hs. *Mol. Phys.* **1974**, *28*, 1305. (d) Kelvin, Lord "Baltimore Lectures"; Clay: London, 1904; pp 618–619. The application of this terminology to geometric objects is sanctioned by Kelvin's statement: "For example, let the given bodies be halves (oblique or not oblique) of any parallelepiped on the two sides of a dividing plane through a pair of parallel edges. The two halves are homochirally similar." (e) Ruch, E. *Acc. Chem. Res.* **1972**, *5*, 49. Ruch, E. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 65.

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