Since many problems of chemical interest involve differences in properties rather than the properties themselves, this is of significant value.

It is also interesting that the success or failure of the different molecular properties seems to be interrelated. Take the example of BF, where the predicted bond length is too long by 0.285 Å, and the predicted dipole moment is −1.33 *vs.* the SCF moment of +0.95. The calculated dipole moment at the experimental bond distance is +0.87.

Table V gives predicted bond angles for a series of AB_2 molecules using experimental A–B bond distances. Comparison is with CNDO/2 values, as the INDO values have not been published. Agreement is satisfactory for all but the AF_2 molecules, where the predicted angles are more than 10° too small. This seems to be the result of the rapid increase of the potential attraction of one fluorine nucleus for an electron around the other fluorine nucleus upon a decrease in bond angle. These nuclear attraction terms increase the diagonal elements of the core Hamiltonian and thereby increase the off-diagonal elements as calculated by expression 10.

Recent work by Boyd and Whitehead[11] has presented a new CNDO method with much improved geometries, energies, and force constants. Their method includes 72 adjustable parameters for the first row alone, however, two for each different A–B bond. We have consequently chosen to compare our results with those of the original INDO method, since it and our method both have only eight freely adjustable parameters, one for each atom.

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(11) R. J. Boyd and M. A. Whitehead, *J. Chem. Soc., Dalton Trans.*, 73, 78, 81 (1972).

Photoelectron Spectra and MINDO–SCF–MO Calculations for Adamantane and Some of Its Derivatives[1a]

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Abstract: The high-resolution photoelectron spectra of adamantane and many of its derivatives have been determined. Eight ionization bands for adamantane are predicted by the MINDO–SCF–MO method to lie in the range 8–18 eV of the photoelectron spectrum. All of the eight bands have been identified and assigned to the appropriate molecular energy levels. The Jahn–Teller effect has been shown to be nonexistent in the degenerate ionic states of the highly symmetric adamantyl radical cation. Limited interpretations have been given for the complex photoelectron spectra of the derivatives of adamantane. In particular, the substituent effects on the ground ionic state corresponding to the highest occupied molecular orbital have been studied. The highest occupied MO of adamantane, 1-methyladamantane, 1-bromoadamantane, 2-bromoadamantane, 1-chloroadamantane, 2-fluoroadamantane, and 1-adamantane carboxylic acid is σ bonding. For methyleneadamantane the first ionization process corresponds to removal of an electron from an MO which is largely π in character. The first ionization band in the photoelectron spectra of 1-adamantanol, 2-adamantanol, adamantanone, and 2,6-adamantanedione has been assigned to a nonbonding MO primarily confined to oxygen, although in each case the "lone pair" appears to be substantially delocalized.

Adamantane is of particular interest in chemistry because of its rigid, relatively strain free diamondoid structure (Figure 1). For this reason, considerable effort has been devoted to elucidating its chemical properties.[2] The derivatives of adamantane also have been studied quite extensively,[2] and a number of interesting observations concerning adamantyl carbonium ions have been reported.[3] It generally is acknowledged that methyl groups are electron donors when attached to carbons which are sp or sp^2 hybridized, but Kwart and Miller[4] have contended that methyl groups attached to sp^3 hybridized carbons in saturated molecules can be electron withdrawing. The solvolysis work of Fort and Schleyer[3] on a series of methyl-substituted 1-adamantyl bromides supports this contention. Progressive substitution of methyl groups at the remaining bridgehead positions of 1-bromoadamantane progressively retards the solvolysis rate in ethanol.[3]

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(1) (a) A preliminary account of part of this work was presented at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, Physical Abstract 107; (b) Cleveland State University and the Chemistry Program Office, Office of Naval Research, Arlington, Virginia 22217; (c) Case Western Reserve University; (d) Kent State University.

(2) For example, see R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, 64, 277 (1964), and the 149 references cited therein.

(3) For example, see R. C. Fort, Jr., and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 86, 4194 (1964), and references cited therein.

(4) H. Kwart and J. L. Miller, *J. Amer. Chem. Soc.*, 83, 4552 (1961).

However, even when the methyl group is attached to an sp^3 carbon, the predominant chemical evidence indicates that it is an electron donor. In the current work the photoelectron spectra of adamantane and a large number of derivatives of adamantane have been studied to ascertain the nature of the substituent effects on the gas phase radical cations. Photoelectron spectroscopy should be reasonably definitive here because electron donors stabilize the ionic state resulting from the removal of an electron from the highest occupied molecular energy level, and thus lead to a decreased adiabatic first ionization potential for the derivative (relative to the unsubstituted molecule). On the other hand, electron-withdrawing substituents destabilize the ionic state and lead to a higher adiabatic first ionization potential.

The only reported determinations of the photoelectron spectra of adamantane or any of its derivatives were the low-resolution studies of Dewar and coworkers[5,6] and a recent preliminary communication concerning the high-resolution spectra of adamantane and 1-bromoadamantane.[7] The present work repeats some of the early low-resolution studies,[5,6] but it considers a number of "new" derivatives as well. The MINDO/1-SCF-MO method also has been used to study many of these molecules. This semiempirical procedure, which treats all of the valence electrons of molecules containing H, C, N, and O, has been demonstrated to give accurate ionization potentials, particularly first ionization potentials, for a large variety of molecules.[5,8] A later version of MINDO (MINDO/2)[9] was employed for some of the derivatives.[6] MINDO/2 is more accurate than MINDO/1 for predicting most chemical properties, but the two versions of MINDO are comparable for calculating ionization energies. In all cases Koopmans' theorem was assumed in obtaining the ionization potentials from the calculated molecular orbital energies.

Because of its high symmetry (T_d), adamantane is a particularly interesting molecule to study by photoelectron spectroscopy. The molecular formula of adamantane is $C_{10}H_{16}$. Thus it contains 56 valence shell molecular orbitals, of which 28 are doubly occupied.[10] The MINDO/1-SCF-MO method predicts that 22 of these doubly occupied MO's lie above -21.22 eV and thus are accessible to the 21.22-eV HeI resonance line, which is the most common excitation source employed in uv photoelectron spectroscopy. For a complex molecule having 22 such bands, even the highest resolution photoelectron energy analyzer available could not resolve more than half of the bands between 8 and 21.22 eV in the photoelectron spectrum. But the high symmetry of adamantane makes this molecule unique. MINDO/1 and group theory predict that many of the MO's for adamantane are doubly or triply degenerate, such that only nine distinct ionization bands should appear in a HeI excited photoelectron spectrum. One of the bands is predicted by MINDO/1 to lie above 19 eV and thus was not accessible in this work (see the Experimental Section). All of the remaining eight bands have been identified in the spectrum and assigned to the various MO's of the molecule. Of course, when the T_d symmetry is destroyed by substitution on adamantane, much of the degeneracy is broken, and additional MO's result from the substituents. The photoelectron spectra of such molecules are very complex and can be interpreted only in general terms.

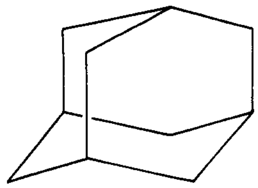

Figure 1. Adamantane ($C_{10}H_{16}$).

The high symmetry of adamantane might be expected to lead to Jahn–Teller distortion of the degenerate ionic states. This could cause a splitting of the photoelectron bands associated with the ^2E, $^2T_1$, and $^2T_2$ ionic states. Evidence of a Jahn–Teller effect has been reported for the photoelectron spectra of several highly symmetric hydrocarbons, including methane,[11] 2,2-dimethylpropane,[12,13] allene,[14] and cyclopropane.[15] As will be discussed later, there was no apparent evidence of Jahn–Teller splitting in the ionization bands for adamantane.

Experimental Section

The photoelectron spectra were recorded by a Varian IEE-15 computerized electron spectrometer. This instrument was designed originally for ESCA studies only, but recent modifications of the excitation source and kinetic-energy analyzer have enabled the measurement of uv photoelectron spectra. The excitation source employed in this study was the 584 Å ≡ 21.22 eV HeI resonance line. The resolution of the analyzer in this work varied between 20 and 35 mV, dependent upon the nature of the sample. For the larger, more nonvolatile compounds, some resolution generally was sacrificed for increased sensitivity. The modified instrument is equipped with an ionization chamber which can be heated for the more nonvolatile compounds, but it is difficult to maintain a constant sample pressure in the ionization chamber when the heater is employed. Since the band positions are quite dependent upon the sample pressure, it was judged best to run the samples at room temperature if possible, thereby sacrificing some sensitivity for increased resolving power. An internal standard (argon or nitrogen) was always run with each sample to minimize error introduced by variations in sample pressure and cleanliness of the analyzer.

In practice, 10–25 scans over the range of 8–18 eV were made for each sample. Each scan was accumulated over a period of 60–200 sec, and the several scans for each sample were coadded by the computer, the resulting compilation being displayed by an X–Y recorder. The scan range of 8–18 eV was so chosen to ensure that the most important first ionization process was always detected and to gain maximum use of the available 2000 channels of the computer. Thus the spectral information in the range 18–21.22 eV was

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(5) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

(6) N. Bodor, M. J. S. Dewar, and S. D. Worley, *J. Amer. Chem. Soc.*, **92**, 19 (1970).

(7) G. D. Mateescu and S. D. Worley, *Tetrahedron Lett.*, 5285 (1972).

(8) S. D. Worley, *Chem. Rev.*, **71**, 295 (1971).

(9) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

(10) All atomic orbitals except the carbon 1s orbitals are considered in the LCAO treatment which gives the "valence" molecular orbitals. The carbon 1s electrons commonly are treated as part of the nuclear core in semiempirical SCF–MO procedures.

(11) For example, see J. W. Rabalais, T. Bergmark, L. O. Werme, L. Karlsson, and K. Siegbahn, *Physica Scripta*, **3**, 13 (1971); *J. Chem. Phys.*, **58**, 3370 (1973).

(12) A. E. Jonas, G. K. Schweitzer, F. A. Grimm, and T. A. Carlson, *J. Electron Spectrosc.*, **1**, 29 (1972).

(13) S. Evans, J. C. Green, P. J. Joachim, A. F. Orchard, D. W. Turner, and J. P. Maier, *J. Chem. Soc., Faraday Trans. 2*, **68**, 905 (1972).

(14) C. Baker and D. W. Turner, *J. Chem. Soc., Chem. Commun.*, 480 (1969).

(15) H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, **51**, 52 (1969).

Table I. Ionization Energies of Adamantane and 1-Bromoadamantane[a]

	Adamantane					1-Bromoadamantane	
	High resolution		Theoretical[b]	Low-resolution		High resolution	
	Adiabatic	Vertical	MINDO/1	Adiabatic[c]		Adiabatic	Vertical
I_1	9.23	9.44	10.07t_2	9.25	I_1	9.30 ± 0.05[d]	9.68
I_2	9.85	10.00	10.72t_1		I_2	9.78	9.88
I_3	10.65	10.97	11.01e	10.69	I_3	10.02	10.16
I_4	11.16	11.36	12.75t_2		I_4	10.45	10.45
I_5	12.72	12.97	12.85t_1	12.90	I_5	(10.70)[e]	(10.70)[e]
I_6	13.15	13.54	14.23t_2		I_6	11.05	11.37
I_7	14.64	14.87	15.04a_1	14.94	I_7	11.51	11.76
I_8	16.76	17.04	16.57a_1	16.79	I_8	12.86	(13.48)[e]
					I_9	13.61	14.07
					I_{10}	14.93	15.18
					I_{11}	(17.07)[e]	

[a] All ionization energies are in eV. [b] MINDO/1 gives a somewhat better correlation with the experimental vertical ionization energies than does MINDO/2. [c] Reference 6; these values may be intermediate between adiabatic and vertical (see text). [d] An error range is quoted because of a broad "foot" at the band onset (see text). [e] These values have rather large uncertainties.

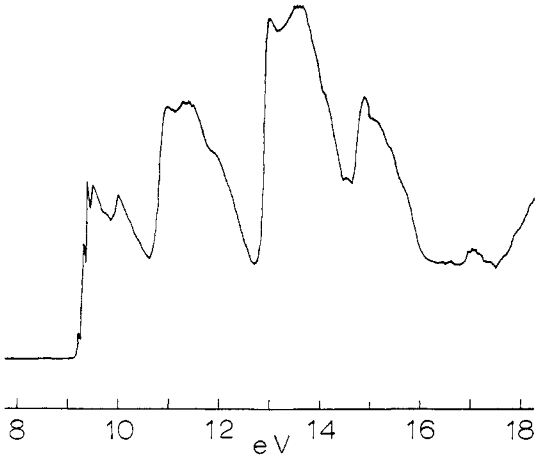

Figure 2. The photoelectron spectrum of adamantane. The excitation source was the 21.22-eV resonance line of He.

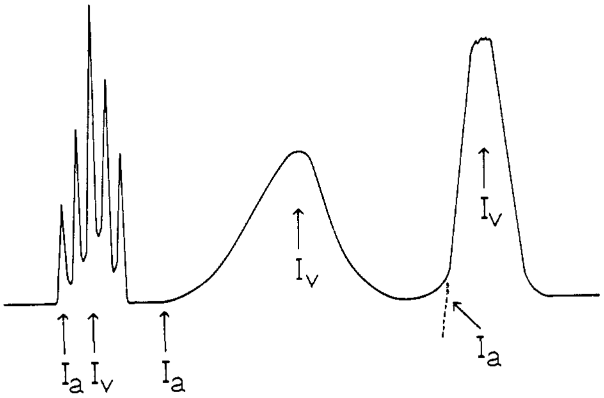

Figure 3. Methods of choosing the adiabatic (I_a) and vertical (I_v) ionization potentials.

sacrificed in order to obtain the best resolution in the range 8–18 eV.

The adamantane derivatives employed in this study either were obtained commercially or were synthesized by standard procedures.[2] The samples were purified by vacuum sublimation or vapor phase chromatography.

Results

The photoelectron spectrum of adamantane is shown in Figure 2. There is a certain amount of ambiguity in the means by which ionization potentials are chosen from the bands of complex, poorly resolved photoelectron spectra. Therefore, it is best to specify the procedure which one uses. The method employed in this work is not claimed necessarily to be the "best" one; nevertheless, it should enable other workers to compare their data with those reported here. When vibrational structure is resolved in an ionization band, as in the first band for adamantane, the means of choosing the adiabatic and vertical ionization potentials are universal. The vibrational peak at lowest binding energy corresponds to the ionic state produced in its ground vibrational level (adiabatic ionization potential), while the most intense vibrational peak at higher energy corresponds to the Franck–Condon transition to the ionic state (vertical ionization potential). When the two most intense vibrational peaks in a band have approximately equal intensity, the vertical ionization potential commonly is chosen as the average binding energy corresponding to the two peaks. However, when the ionization bands are broad and featureless, the means of choosing the adiabatic and vertical ionization energies becomes more arbitrary. For the featureless bands in this work, the adiabatic ionization potential has been assigned to the first change of slope (from the base line) for asymmetric, slowly rising bands and to the extrapolated edge of the more rapidly rising bands (see Figure 3). The vertical ionization potential for such bands has been chosen as the binding energy corresponding to the center of the most intense part of the band; this generally corresponds closely to the binding energy at the most intense point in the band. Of course, substantial error can be introduced when choosing the adiabatic ionization potentials in this manner, particularly when there is a broad "foot" on the leading edge of a rapidly rising band. In such cases a range has been quoted for the adiabatic ionization energies.

The ionization potentials measured in this work from the high-resolution photoelectron spectrum of adamantane are given in Table I. Table I also lists the values obtained in the early low-resolution study[6] and the MINDO/1 orbital energies and symmetries. The experimental high-resolution ionization potentials of 1-bromoadamantane are included for comparison (see the Discussion section). The high- and low-resolution first ionization energies of the various adamantane derivatives in this work and the earlier work,[6] respec-

Table II. First Ionization Energies of Adamantane and Some of Its Derivatives[a]

Molecule	High-resolution I_1		Theoretical[b]		Low-resolution I_1	
	Adiabatic	Vertical	MINDO/1	MINDO/2	Adiabatic[c]	ν, cm^{-1}[d]
Adamantane	9.23	9.44	10.07	9.66	9.25	890
1-CH_3	9.17 ± 0.02	9.55	9.84	9.61	9.24	
2-CH_3			9.88	9.33	9.24	
1,3,5,7-Tetramethyl			9.79	9.55	9.23	
Methylene	8.82	8.89	9.72			1290
1-OH	9.09 ± 0.05[e]	9.51	10.11	9.62	9.23	
2-OH	9.09 ± 0.07[e]	9.52	10.08	9.64	9.25	
2-OH, 2-CH_3			9.97	9.39	9.22	
1-Br	9.30 ± 0.06[e]	9.68				
2-Br	9.31 ± 0.05[e]	9.64				
1-Cl	9.30	9.89				1210
2-F	9.46	9.86				1130
1-COOH	9.34	9.78				
Congressane			9.54	9.20	8.93	
Adamantanone	8.59	8.88	9.79	9.38	8.76	1210
2,6-Adamantanedione	9.06	9.25				550, 1210

[a] All ionization energies are in eV. [b] This work and ref 6. [c] Reference 6; some of these values may be intermediate between adiabatic and vertical (see text). [d] Vibrational spacing, where resolved, in the first ionization band. [e] An error range is quoted because of a broad "foot" at the band onset (see text).

tively, are presented in Table II. Because of the low symmetries of the derivatives, only part of the numerous ionization bands were resolved. Therefore, just the first ionization energies have been given. Some of the particularly significant higher ionization bands for these molecules will be discussed in the text. Table II also lists MINDO/1 and MINDO/2 highest occupied orbital energies for those molecules for which MINDO is parameterized. Vibrational frequencies are tabulated for the bands in which vibrational structure was resolved.

Figure 2 and Table I differ slightly from the data reported in the preliminary communication[7] because the work has been repeated at somewhat higher resolution.

Discussion

Adamantane. Group theoretical considerations indicate that the 58 valence molecular orbitals of adamantane transform under point group T_d in the following manner

$$6a_1 + 4e + 4t_1 + 10t_2$$

Only half of these MO's are occupied in the molecular ground state (in this case, $3a_1 + 2e + 2t_1 + 5t_2$), and MINDO/1 predicts that those accessible in the range 8–18 eV of the current experiment have the following symmetries.

$$2a_1 + 1e + 2t_1 + 3t_2$$

Thus eight ionization bands should be detected below 18 eV in the photoelectron spectrum. In Figure 2 it certainly appears that eight bands are present if one considers the lowest three bands each to represent two ionization processes. Of course, such broad, "split" bands also could be attributed to Jahn–Teller distortion of the ^2E or ^2T ionic states corresponding to a single ionization process. Arguments to be given negate the latter possibility, so it is assumed in the present discussion that all eight of the expected ionization bands were detected.

From Table I it is seen that the MINDO/1 orbital energies are in reasonable accord with the experimental vertical ionization potentials,[16] the average deviation being only *ca.* 0.5 eV. The symmetries of the eigenvectors corresponding to the various eigenvalues calculated by MINDO/1 are given also in Table I. The lowest energy band in the photoelectron spectrum corresponds to ionization processes leading to a $^2T_2$ and a $^2T_1$ ionic state and thus could certainly be subject to Jahn–Teller splitting. The same is true for the second and third bands which are assigned to ^2E, $^2T_2$ and $^2T_1$, $^2T_2$ ionic states, respectively. The last two bands (at highest energy) are both assigned to $^2A_1$ ionic states and cannot be subject to Jahn–Teller distortion.

Table I also gives the low-resolution "adiabatic" ionization potentials for adamantane, which were measured from onsets of diffuse bands.[5,6] Note that only five of the expected eight bands were detected at low resolution, but for those detected, the agreement with the high-resolution data was quite satisfactory. Heilbronner and coworkers[17] have claimed that ionization potentials obtained from low-resolution grid analyzers are really intermediate between adiabatic and vertical. This usually is true for the higher ionization potentials due to band overlapping, but adiabatic first ionization potentials measured by a low-resolution analyzer commonly are quite accurate, as is the case for adamantane. In general, only when extensive geometry reorganization occurs upon ionization is the low-resolution analyzer not sufficiently sensitive to detect adiabatic first ionization potentials.

Vibrational structure was resolved in the first ionization band of the high-resolution spectrum of adamantane. The vibrational spacing corresponded to a frequency of 890 cm^{-1} which could be attributed to a C–C stretching mode for the lowest energy $^2T_2$ ionic state.

Jahn–Teller Effect. As stated earlier, it is possible that the split bands in the photoelectron spectrum of adamantane should be attributed to Jahn–Teller dis-

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(16) Since Koopmans' theorem does not provide for geometry reorganization upon ionization, calculated orbital energies should be compared with vertical ionization potentials (as opposed to adiabatic values).

(17) C. Batich, P. Bischof, and E. Heilbronner, *J. Electron Spectrosc.*, 1, 333 (1972).

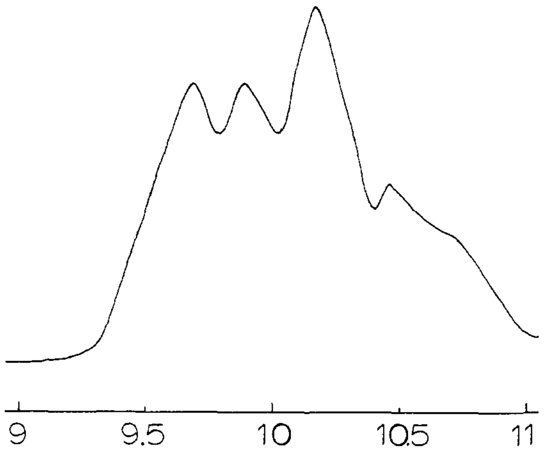

Figure 4. The 9-11-eV region of the photoelectron spectrum of 1-bromoadamantane.

tortion instead of to separate ionization processes. There are four arguments against Jahn-Teller distortion which can be presented.

(1) For ionic states subject to Jahn-Teller distortion, the symmetry of the state is lowered, causing a destruction of degeneracy and consequent production of two or more new ionic states. A substantial geometry reorganization should accompany this process. Adamantane is a rigid, nearly stain-free molecule. Intuitively, it is unlikely that the geometry of the adamantyl radical cation could be significantly altered from that of adamantane.

(2) As mentioned previously, the adiabatic first ionization potentials determined at low resolution agree quite well with the more accurate values measured at high resolution unless substantial geometry reorganization occurs. Extensive geometry changes upon ionization generally lead to low Franck-Condon factors (probabilities) for production of the ionic state in its ground vibrational level. In this case a photoelectron spectrometer having low sensitivity may fail to detect the 0-0 adiabatic transition; the apparent "adiabatic" ionization potential then corresponds to a transition to a higher vibrational level of the ionic state. Such anomalies are most prevalent for molecules for which the existence of a Jahn-Teller effect has been proved (*e.g.*, high resolution/low resolution (eV):methane, 12.55[11]/12.98;[5] allene, 9.69[14]/9.83;[5] cyclopropane, *ca.* 9.8[15]/10.06;[5] 2,2-dimethylpropane, 10.21,[12] 10.25[13]/10.40[5]). On the other hand, for highly symmetric molecules for which the Jahn-Teller effect is weak, or nonexistent, the low-resolution and high-resolution adiabatic first ionization potentials are virtually the same (*e.g.*, benzene, 9.25[18]/9.24[5]). The low-resolution and high-resolution values of the adiabatic I_1 for adamantane (Table I) agree to within 0.02 eV. Thus, it is doubtful that the first band in Figure 2 exhibits Jahn-Teller splitting. The low-resolution "adiabatic" ionization potentials corresponding to I_3 and I_5 in the high-resolution spectrum are too high by 0.04 and 0.18 eV, respectively. This is due probably to band overlapping, as suggested by Heilbronner and coworkers,[17] rather than to Jahn-Teller distortion. Note that the low-resolution value corresponding to the high-resolution I_7 is 0.3 eV too large; yet I_7 corresponds to a $^2A_1$ ionic state which cannot be subject to Jahn-Teller distortion.

(3) The difference in energy between the vertical and adiabatic ionization potentials ($I_v - I_a$) for a particular ionization band commonly is considered to be indicative of the extent of geometry reorganization upon ionization. A band in the photoelectron spectrum which contains only one vibrational component may be attributed to ionization of a nonbonding MO. For such a process $I_v - I_a$ is zero, and geometry reorganization upon ionization is minimal. However, a large $I_v - I_a$ implies that the electron has been removed from a bonding or an antibonding MO accompanied by extensive geometry reorganization in the ionic state. Table I includes the values of I_a and I_v for 1-bromoadamantane. This derivative of adamantane has C_{3v} molecular symmetry with its highest occupied MO transforming under irreducible representation e and is thus subject to possible Jahn-Teller distortion in its ^2E ionic states. The magnitude of splitting between the Jahn-Teller components of an ionization band ($I_{2v} - I_{1v}$ in Table I if Jahn-Teller distortion is present) should be proportional to the extent of geometry reorganization also. From Table I it is seen that $I_{1v} - I_{1a}$ for adamantane is 0.21 eV, while $I_{1v} - I_{1a}$ for 1-bromoadamantane is *ca.* 0.38 eV, implying that geometry reorganization upon ionization is more significant for the derivative. On the other hand, $I_{2v} - I_{1v}$ for adamantane is 0.56 eV, while $I_{2v} - I_{1v}$ for 1-bromot adamantane is only 0.20 eV, and even $I_{3v} - I_{1v}$ for th- derivative is only 0.48 eV. The implication now is thae the geometry change is greater for adamantane *if* Jahn-Teller splitting is responsible for $I_{2v} - I_{1v}$. The obvious contradiction here provides additional evidence against Jahn-Teller distortion for adamantane, because beyond all doubt, the $I_{1v} - I_{1a}$ in Table I refers to a single ionization process.

(4) Upon substitution of Br at the bridgehead (1) position of adamantane, the T_d symmetry is lowered to C_{3v}. If one assumes that the first "split" band in the adamantane spectrum does correspond to production of $^2T_2$ and $^2T_1$ ionic states, a similar broad band in the spectrum of 1-bromoadamantane should correspond to two ^2E states, a $^2A_1$ state, and a $^2A_2$ state. Furthermore, the photoelectron spectra of compounds containing Br generally have "lone-pair" ionization bands near 10.5 eV (*e.g.*, bromobenzene, 10.65 eV;[19] bromine, 10.51 eV;[20] bromoethane, 10.46 eV[21]). The first broad band in the photoelectron spectrum of 1-bromoadamantane is shown in Figure 4. There are clearly four distinct ionization processes within this band plus a slight shoulder on the high-energy edge. Thus all five bands which would be expected in the 9-11-eV region of the photoelectron spectrum of 1-bromoadamantane can be accounted for *if* Jahn-Teller distortion is assumed to be negligible for these molecules.

Adamantane Derivatives. In the early low-resolution work on the derivatives of adamantane[6] it was concluded that there was little or no substituent effect on

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(18) A. D. Baker, C. R. Brundle, and D. W. Turner, *Int. J. Mass Spectrom. Ion Phys.*, **1**, 443 (1968).

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

(20) A. B. Cornford, D. C. Frost, C. A. McDowell, J. L. Ragle, and I. A. Stenhouse, *J. Chem. Phys.*, **54**, 2651 (1971).

(21) J. A. Hashmall and E. Heilbronner, *Angew. Chem., Int. Ed. Engl.*, **9**, 305 (1970).

the first ionization potentials (I_1 in Table II), for most of the molecules. Only for congressane and adamantanone were appreciable shifts detected. For congressane, the diamondoid skeleton itself has been increased by four carbon atoms; such increases in molecular size always lead to lower values of I_1. For adamantanone, molecular strain has been increased relative to adamantane which should lead also to a lower ionization potential, as has been observed. But it will be shown that the first ionization process for adamantanone can be attributed to a carbonyl "lone-pair" electron.

The current high-resolution work on the various derivatives (Table II) does indicate that there is some substituent effect present, although it seems to be abnormally weak in most cases. One also notes that the substituent effect is not always in the same direction for the corresponding adiabatic and vertical first ionization potentials. For example, the methyl group appears to act as a weak electron donor when substituted at the bridgehead position of adamantane if one considers the high-resolution adiabatic I_1 values of adamantane and 1-methyladamantane. The same conclusion is reached from the MINDO/1 and MINDO/2 orbital energies (Table II) which normally should correlate best with the vertical ionization potentials. But if the experimental vertical values of I_1 for adamantane and 1-methyladamantane are considered, methyl appears to be a withdrawing substituent. The latter is the conclusion reached by Fort and Schleyer[3] in their solvolysis study (see the introductory section). Photoelectron spectroscopists have correlated substituent shifts with both adiabatic and vertical ionization energies, so it is difficult to arrive at a meaningful conclusion here. It seems reasonable to consider the shift of the ground vibration level of the ionic state upon substitution, *i.e.*, the adiabatic ionization potentials, but it is also logical to consider the change in geometry reorganization upon ionization caused by the substituent, as indicated by the relative vertical ionization potentials. Although the current work cannot tie down definitely the nature of the 1-methyl-substituent effect on the adamantyl radical cation, it does show that the effect is quite weak. It should be noted that the methyl-substituent effect also is quite weak for methylcyclohexane, for which I_{1a} is only 0.03 eV lower than I_{1a} for cyclohexane.[22]

From the data in Table II is is evident that MINDO/2 gives a somewhat better account of the absolute orbital energies than does MINDO/1; however, MINDO/1 seems to order the substituent shifts more accurately (when compared to the vertical ionization potentials). The almost nonexistent substituent shifts measured from the low-resolution spectra[6] must be a consequence of the lower sensitivity of the grid analyzer relative to the high-resolution electrostatic analyzer.

Table II shows the substituent in 1-bromoadamantane, 2-bromoadamantane, 1-chloroadamantane, 2-fluoradamantane, and 1-adamantanecarboxylic acid acts as an inductive electron-withdrawing agent, regardless of whether the adiabatic or vertical I_1 is considered. The 1210- and 1130-cm^{-1} vibrational frequencies measured from the I_1 bands of 1-chloroadamantane and 2-fluoroadamantane, respectively, could be attributed to a halogen-influenced CH$_2$ wagging mode for the ions. A sharp, intense band appeared at 10.56 eV in the spectrum of 1-chloroadamantane. This band can be assigned to Cl "lone-pair" ionization. Turner and coworkers[19] have detected Cl "lone-pair" ionizations for a large number of chloro compounds in the range 10.5–12.5 eV; 1-chloroadamantane thus seems to have an extremely low first Cl nonbonding ionization energy. A second band at *ca.* 11.5 eV in the spectrum of the chloro derivative is probably also due to a Cl "lone-pair" ionization. A nonbonding ionization for 1-bromoadamantane and for 2-bromoadamantane appears at *ca.* 10.5 eV, but no evidence for nonbonding ionizations was found in the spectrum of 2-fluoroadamantane. The substituent effect for the latter compound (0.23 eV adiabatic, 0.42 eV vertical) seems rather weak in view of the massive (2.5–4.0 eV) effects commonly observed for saturated hydrocarbons upon complete fluorine substitution ("perfluoro effect").[23] Substitution of one F on ethylene causes an increase of 0.94 eV in its first σ ionization potential.[23]

For five of the derivatives listed in Table II the highest occupied MO is primarily associated with the substituent rather than the diamondoid moiety. Since OH is an inductive electron-withdrawing group for saturated systems, the adiabatic and vertical first ionization potentials of 1-adamantanol and 2-adamantanol should be higher than I_a and I_v, respectively, for adamantane. Yet the I_a values for both alcohols are *ca.* 0.14 eV *lower* than is that for adamantane. The values of I_v for the alcohols are somewhat higher, as expected. The MINDO methods predict that the highest occupied MO for both of the alcohols is confined largely to oxygen. Thus it is apparent that the highest occupied MO is primarily nonbonding, although the "lone-pair" is delocalized extensively, as is evidenced by the rather broad I_1 band. The apparent "vertical I_1" may correspond to the highest occupied MO of the "ring." MINDO/1 predicts that the highest occupied MO of methyleneadamantane is essentially of π type from the isolated double bond. This prediction is substantiated by the photoelectron spectrum of the molecule. The change in I_1 relative to adamantane is quite large (-0.41 eV adiabatic, -0.55 eV vertical), and a vibrational frequency of 1290 cm^{-1} is evident. This vibrational frequency can be assigned readily to the C=C stretching mode for the ionic state. Frost and Sandhu[24] have shown that 1,1-dimethyl substitution on ethylene causes a decrease in I_1 from 10.56 to 9.21 eV. The adamantyl moiety would be expected to cause an even larger decrease in the π ionization potential of ethylene because of the size of adamantane and because of the added strain which would be introduced at the sp^2 carbon of the double bond. This is observed, for I_1 of methyleneadamantane is 8.82 eV. Chadwick, Frost, and Weiler[25] have studied the photoelectron spectra of a series of alicyclic ketones, the largest of which was cyclooctanone. They concluded that the highest occupied MO for these molecules was essentially nonbonding. The nonbonding vertical ionization potentials and "σ onsets" decreased steadily as the size of the

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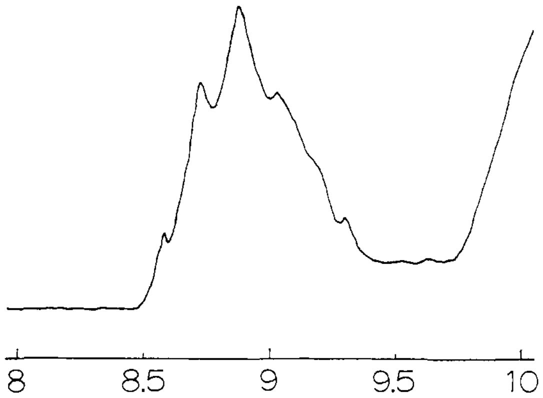

Figure 5. The 8–10-eV region of the photoelectron spectrum of adamantanone.

molecular skeleton increased; the values for cyclooctanone were 9.09 and 10.3 eV, respectively. Vibrational structure was observed in the first band also, and frequencies of 740 and 1267 cm^{-1} were reported.[25] The photoelectron spectrum of adamantanone in the current work exhibited vibrational structure in the first band (see Figure 5) with $\nu = 1210$ cm^{-1}, which can be assigned to the C=O stretch for the ion. The vertical I_1 adamantanone is 8.88 eV which is lower than that[25] for cyclooctanone, as would be expected for the larger ring system. Furthermore, MINDO/1 predicts that the highest occupied MO for adamantanone is located predominantly on the carbonyl oxygen, although there is predicted substantial delocalization of this MO throughout the molecule. Thus it is quite certain that I_1 for adamantanone corresponds to an oxygen "lone-pair" electron. The I_2 for adamantanone (9.74 eV) must then refer to the inductively destabilized "σ onset." It should be emphasized, however, that the "lone-pair" MO corresponding to I_1 is substantially delocalized for this ketone, as can be inferred from the rather extensive vibrational structure and the low value of ν for the ionic state. The first band in the spectrum of 2,6-adamantanedione also exhibits vibrational structure with $\nu = 1210$ cm^{-1} (and also 550 cm^{-1}). The adiabatic and vertical first ionization potentials of this diketone are several tenths of an electron volt higher than those for adamantanone but lower than the values for adamantane. This ionization process can be assigned once again to the nonbonding MO confined mainly on oxygen. However, the rather large shift to higher ionization energy shows that this "nonbonding" MO is quite delocalized, and the ionic state is destabilized inductively by the presence of a second carbonyl group.

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Photochemistry of Propionaldehyde in Solution Studied by Electron Spin Resonance and CIDNP

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Abstract: The photolysis of propionaldehyde in solution has been studied by means of electron spin resonance and proton nuclear magnetic resonance spectroscopy. The nmr spectrum obtained during irradiation indicates that a number of compounds are formed with their protons spin polarized. Using a radical pair model to account for the nuclear spin polarization, it is possible to suggest photochemical reaction steps to account for the observed nmr spectrum. By means of radical trapping experiments using carbon tetrachloride, it is possible to decide which components are formed by primary photochemical steps and which are derived by subsequent steps. Quenching by nitric oxide supports the proposal that the primary steps occur *via* the excited triplet electronic state. Among these steps are α cleavage and bimolecular hydrogen abstraction.

Recently the photochemistry of acetaldehyde[1] and pivalaldehyde[2] in solution was studied by means of chemically induced dynamic nuclear spin polarization (CIDNP). For acetaldehyde, the observed spin polarization was explained by a bimolecular primary step in which an acetaldehyde molecule in an excited triplet state removes the carbonyl hydrogen from a ground state acetaldehyde molecule. In contrast, the CIDNP results for pivalaldehyde were explained by a unimolecular primary step which involved α cleavage *via* a triplet excited state to give the *tert*-butyl and formyl radicals.[3] Furthermore, variation of the solvent seems to have no effect on the outcome for either of these compounds.

For these reasons we have undertaken a study of the photochemistry of propionaldehyde to ascertain if

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