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The Tropyl Cation (c-$C_7H_7^+$) and the Tropyl Radical (c-C_7H_7)

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Ab initio molecular orbital and density functional theory calculations are performed on the tropyl cation (c-$C_7H_7^+$) and the neutral tropyl radical (c-C_7H_7). For the tropyl cation the optimized geometry is found to have D_{7h} symmetry, in agreement with experimental results. The harmonic vibrational frequencies for the cation are calculated at various levels of theory and compared to previous assignments, derived from experimental work. It is found that there are a number of discrepancies and the assignments are updated accordingly. Electronic excitation energies for the cation are then calculated. The tropyl radical ($^2B_1$) is calculated to have a C_{2v} equilibrium geometry. The harmonic vibrational frequencies are also calculated for this species. Finally, the first adiabatic and vertical ionization energies for c-C_7H_7 are calculated and found to be in excellent agreement with experiment.

I. Introduction

A. Vibrational Frequencies. The tropyl cation, $C_7H_7^+$, is of importance in all three of the main branches of chemistry: in organic chemistry as an organic hydrocarbon radical cation,[1] where its formation is in competition with the isomeric benzyl cation;[2,3] in inorganic chemistry as a stable ligand;[4−6] and in physical chemistry as a prototypical example of an aromatic hydrocarbon cation.[7]

The vibrational spectroscopy of the tropyl cation has been a matter of some debate over the years, with information coming from spectroscopic studies of organic solutions[8−10] and inorganic solutions[5,6] and in the gas phase using resonance-enhanced multiphoton ionization (REMPI)[11] spectroscopy and HeI photoelectron spectroscopy (PES).[12] The high-symmetry D_{7h} of the tropyl cation leads to only a relatively small number of the 36 vibrational modes being either infrared or Raman active (in fact, there is a mutual exclusion of infrared and Raman activity, although the D_{7h} point group does not have inversion as a symmetry operation).[10,13] Although the frequencies of the four infrared-active vibrations and the seven Raman-active vibrations seem to be reasonably well-established (vide infra), the vibrations that are neither infrared nor Raman active appear not to have clear assignments. These assignments have been inferred both from combination bands, as well as from studies where the environment of the $C_7H_7^+$ has been lowered in symmetry, leading to a relaxation of the selection rules (vide infra*)*. The most complete assignment of the vibrational frequencies of the tropyl cation appears to be that of Sourisseau and Hervieu,[5] although this assignment is not complete. Additionally, there has been some recent controversy in the assignment of the vibrational frequencies, with disagreement from a HeI PES study[12] of the C_7H_7 radical, where vibrational structure was obtained, and the recent REMPI spectroscopic study.[11] The REMPI study gained information on highly excited electronic states, which were assigned as Rydberg states therein. Since the spectroscopic properties of Rydberg states should be very close to those of the cationic core, some implications were made concerning the vibrational assignment of the cation; in particular, reassignments of some of the vibrational features seen in the HeI PES were made.

Part of the aim of the present work was to calculate reliable values of the harmonic frequencies, to try to clarify the assignment of the vibrational frequencies of the tropyl cation. In addition, the vibrational frequencies of the neutral tropyl radical are calculated: there appear to be no experimental values.

B. Low-Lying Electronic States of the Tropyl Cation and the Ionization Energy. The tropyl cation has a closed-shell $\tilde{X}\ ^1A_1'$ electronic configuration; thus, excited states are going to have triplet or singlet spin multiplicity. The earliest information on the excited states appears to be that of von E. Doering and Knox,[8] who obtained a UV spectrum in an aqueous solution, demonstrating a band in the range 247−275 nm. Thrush and Zwolenik[14] obtained the UV absorption spectrum of the tropyl radical in a flash photolysis experiment; they identified a series of bands (∼217−260 nm), which were assigned to Rydberg series, and so were able to extrapolate to obtain the adiabatic ionization energy (AIE) as 6.237 eV, which agreed with earlier values of 6.41 eV (calculated by Streitweiser[15]), and 6.6 ± 0.1 eV, measured using mass spectrometry by Harrison et al.[16] Two additional pieces of experimental evidence for the position of electronically excited states of c-$C_7H_7^+$ exist. The first comes from a photoionization study by Elder and Parr,[17] who identified a shoulder in their photoionization efficiency (PIE) curve at 6.75 eV and tentatively associated it with an excited state. The onset of their PIE curve gave a measure of the AIE as 6.236 ± 0.005 eV, which then leads to an excited state at 0.51 eV. The photoelectron spectrum reported by Koenig and Chang[14]

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indicated the presence of an excited state of the cation at an ionization energy of 9.63 eV, which gives an excitation energy of 3.35 eV, when combined with the first ionization energy measured by them as 6.28 eV. Theoretical calculations have been used to predict the position of the excited states of the tropyl cation. Murrell and Longuet-Higgens[18] and Gallup and Norbeck[19] used semiempirical SCF molecular orbital theory, obtaining some agreement with the position of the band observed by von E. Doering and Knox.[8] Clearly the basis sets used in those studies are rather small, owing to the limited computational power available when the work was performed and the large size of the tropyl cation. For the present work, it seemed appropriate to use the relatively inexpensive method of configuration interaction with single excitations (CIS) with a reasonable basis set in order to obtain more reliable values for the positions of excited states of the tropyl cation. In addition, the adiabatic and vertical ionization energies of *c*-C_7H_7 are calculated and compared to the experimental values.

II. Theoretical Methods

For the tropyl cation, calculations were performed at the HF and MP2 levels of theory in the first instance using the 6-31G** basis sets (not reported herein). Further calculations at the HF and MP2 level were performed using the 6-311G(2d, p) basis set. For these and all other calculations reported in this work (cation and neutral), analytic gradient methods are used for geometry optimization, and analytic second derivatives are used for the calculation of harmonic vibrational frequencies. (For a molecule with a large number of degrees of freedom, use of numerical derivatives is impracticable.) In addition, the B3LYP hybrid density functional[20] was employed. Calculations using the 6-311G(2d,p) basis set were initially employed, to be able to compare the results with those of the MP2 method; further, B3LYP/cc-pVTZ calculations were performed. CIS/6-311++G** calculations were also employed at the MP2/6-31G** geometry in order to gain some insight into the position of both the electronically excited singlet and triplet states.

For the neutral tropyl radical, calculations were performed on the $\tilde{X}^2B_1$ ground electronic state of the C_{2v} species. Note that calculations involving D_{7h} symmetry were attempted using the GRHF approach with the GAMESS-UK[21] package; however, convergence problems were encountered. In addition, calculations on the $^2A_2$ state were performed at the ROHF/6-31G** level of theory using GAMESS-UK and additionally at the MP2/6-31G** and B3LYP/6-31G** levels using unrestricted wave functions; these indicated that this was not a minimum, but a saddle point. Consequently, it was the $^2B_1$ state on which most of the calculations were performed. The second derivative calculations indicated that the calculated geometries were minimum energy structures for this state, but that the use of UHF wave functions was leading to severe spin contamination ($\langle S^2\rangle = 1.2$, rather than 0.75). To see the effect that this was having on the calculated harmonic frequencies and geometries, ROHF calculations were performed using GAMESS-UK to compare with the UHF calculations. (Unfortunately, ROMP2[22] calculations were not possible, since for these analytic second derivatives were not available, and as mentioned above, numerical derivative calculations would have been impracticable.) A notable observation was made concerning B3LYP calculations on the $^2B_1$ state: although unrestricted wave functions were employed, the spin contamination appeared to be much less serious: $\langle S^2\rangle \sim 0.77$. In addition, to test the reliability of the ROHF results, CASSCF(5,5) and CASSCF(7,7) calculations were performed using the 6-31G** basis set. The active space for these calculations were chosen to consist of the out-of-plane Cpπ molecular orbitals of a_2 and b_1 symmetries. For the CASSCF(7,7) calculations, all seven Cpπ molecular orbitals were included in the active space.

Finally adiabatic ionization energies (AIEs) and vertical ionization energies (VIEs) were calculated at various levels of theory, by performing single-point energy calculations at the (U)MP2/6-31G** geometries of the neutral and cationic states.

Unless stated otherwise, all of the above calculations were performed using Gaussian94.[23]

III. Results and Discussion

a. Geometries of *c*-$C_7H_7^+$ and *c*-C_7H_7. The geometry of $C_7H_7^+$ is known to be of D_{7h} symmetry: this is evinced by its known aromaticity and the appearance of its infrared and Raman spectra. Actual structural determinations have been rather sparse, however, with the only determinations appearing to be those from X-ray diffraction of inorganic compounds, in which the $C_7H_7^+$ moiety is stabilized.[4] These give a value of 1.40 ± 0.02 Å for the C−C bond length, with a C−H distance of 1.09 ± 0.02 Å. The calculated D_{7h} structure (Table 1) is thus in good agreement with these results, as are the calculated C−C and C−H bond lengths.

The tropyl radical, in D_{7h} symmetry, is subject to the Jahn−Teller effect, having an electron in a pair of degenerate orbitals; thus, the geometry may be a static C_{2v} structure, or a dynamic D_{7h} structure, depending on the magnitude of the Jahn−Teller interaction. The experimental evidence for the geometry of the neutral tropyl radical comes from ESR spectroscopy in crystals and matrixes[24] and in liquids;[25] these indicated that the seven hydrogen atoms are equivalent. Caution must always be taken, however, with non-gas-phase geometries, as crystal, matrix, and solvent effects may all affect the observed geometry; although, in general, these tend to distort the geometry *away* from symmetrical. We note in passing that the C_5H_5 (cyclopentadienyl) radical has been shown to have a dynamic D_{5h} symmetry for the $\tilde{X}^2E_1''$ electronic state.[26] As was noted in the Theoretical Methods section, the two C_{2v} components of the $\tilde{X}^2E_1''$ state of the tropyl radical were studied, with the $^2A_2$ component being calculated as a saddle point but the $^2B_1$ state being a minimum. The energies of these two states were, however, very close in energy (0.065 eV, at the MP2/6-31G** level), with the $^2B_1$ state the lower.

As may be seen from Table 3, the calculated geometries of the neutral radical at various levels of theory are in reasonable agreement with each other, even when spin-contaminated wave functions were used. This is encouraging and allows us to have some confidence in the use of the MP2/6-31G** geometry for the calculation of the AIEs and VIEs. The calculated C−C bond lengths show significant deviations away from D_{7h} symmetry. There are no experimental structural determinations of the geometry of the tropyl radical, to the authors' knowledge, except for the ESR studies, noted above.

b. Vibrational Frequencies of *c*-$C_7H_7^+$ and Assignment. The assignment of the vibrational modes given in the first column of Table 1 is based on a number of facts. It was unfortunately not possible simply to assign the symmetry of the vibrational mode by consideration of the calculated normal coordinate displacements, since for the degenerate modes in particular, the use of C_s symmetry for the calculation, by Gaussian94, made it impossible to decide the precise symmetry of some of the vibrational modes. The ′ and ″ nature of the modes was very straightforward to determine, as was the A and E symmetry. For the A modes, it was also fairly straightforward

TABLE 1: Calculated Geometric Parameters and Harmonic Vibrational Frequencies for *c*-$C_7H_7^+$

quantity	HF/6-311G(2d,p)	MP2/6-311G(2d,p)	B3LYP/6-311G(2d,p)	B3LYP/cc-pVTZ	IR/Raman activity (exptl)[c] [calcd][a]	experiment[a]
energy/E_h	−268.96215	−269.93992	−270.74703	−270.76740		
r_{C-H}	1.0747	1.0868	1.0849	1.0832		1.09 ± 0.02
r_{C-C}	1.3842	1.3974	1.3929	1.3923		1.40 ± 0.02
ω_{14} or ω_{20}	245.0	214.7	219.7	221.8	×	238[b]
ω_{12}	468.1	429.6	440.8	440.7	R (m) [6.0]	433[c]/430[d]
ω_{13} or ω_{19}	604.9	557.9	562.0	566.9	×	562[b]
ω_4	723.8	656.5	659.9	663.3	IR (s) [93.6]	633[c]/658[c]/648[d]
ω_2	928.9	869.3	876.0	878.0	R (vs) [75.0]	868[c]/869[d]
ω_{18}	935.7	884.3	887.9	892.6	×	892[d]
ω_8	970.7	912.2	903.0	903.8	R (w) [0.04]	925[c]
ω_7	1073.2	1005.4	1009.7	1012.4	IR (mw) [6.8]	992[c]/993[d]
ω_{13} or ω_{14} or ω_{19}	1161.5	1043.2	1057.9	1066.0	×	
ω_{13} or ω_{19}	1184.1	1050.7	1079.2	1088.9	×	
ω_{11}	1333.6	1248.9	1251.7	1254.7	R (mw) [1.5]	1210[c]/1224[d]
ω_{17}	1369.5	1313.2	1312.1	1313.6	×	
ω_3	1561.5	1436.2	1450.0	1449.4	×	
ω_{16}	1592.5	1511.1	1522.3	1521.8	×	
ω_6	1640.2	1623.1	1549.2	1554.7	IR (vs) [56.9]	1477[c]/1477[d]
ω_{10}	1765.8	1688.2	1630.1	1631.0	R (m) [19.9]	1594[c]/1596[d]
ω_{15}	3325.7	3183.1	3161.8	3164.8	×	
ω_9	3336.9	3193.0	3170.8	3174.0	R (s) [124.3]	3045[c]/3040[d]
ω_5	3349.0	3202.7	3180.4	3183.8	IR (s) [1.2]	3020[c]/3020[d]
ω_1	3354.8	3207.5	3185.5	3189.0	R (s) [399.5]	3085[c]/3072[d]

[a] The IR intensities (km mol^{-1}) were consistent at all the levels of theory but are presented here at the HF/6-311G(2d,p) level of theory; the Raman intensities ($Å^4$ amu^{-1}) were calculated at the HF/6-311G(2d, p) level of theory. The experimental intensities are representative of observations reported in the quoted references—these values differ slightly between references, depending on the precise environment of the $C_7H_7^+$ moiety. The symmetries of the vibrations may be obtained from Table 2. The experimental geometry comes from X-ray diffraction studies; see, for example, ref 4. [b] From ref 6. [c] From ref 10. [d] From ref 5.

TABLE 2: Vibrational Numbering Scheme

no. of vibration	symmetry	no. of vibration	symmetry
1	A_1'	11	E_2'
2	A_1'	12	E_2'
3	A_2'	13	E_2''
4	A_2''	14	E_2''
5	E_1'	15	E_3'
6	E_1'	16	E_3'
7	E_1'	17	E_3'
8	E_1''	18	E_3'
9	E_2'	19	E_3''
10	E_2'	20	E_3''

to determine whether a mode was A_1 or A_2. For the E modes, varying degrees of difficulty were encountered. For the E′ modes, the symmetry (E_1', E_2', or E_3') could be obtained from whether the mode was IR or Raman active (or not); for the E″ modes much difficulty was encountered, and the assignments (where possible) are based upon comparison with the previous assignments, discussed below. As may be seen, there are still a few vibrational modes in Table 1 whose numbering is uncertain. The symmetry and numbering of the vibrations are given in Table 2; these are taken from refs 5 and 6. (Note that in refs 5 and 6, simple descriptions of the vibrations are given; however, the normal coordinates obtained in the present work suggest that these descriptions are an oversimplification, and much mixing occurs.)

(i) Infrared-Active Modes. In Table 1 are listed the 20 calculated vibrational frequencies for the molecular vibrations of the D_{7h} tropyl cation (there are 36 vibrational modes altogether, including degeneracies). As may be seen, the values calculated using both the MP2 and the B3LYP approaches are reasonably consistent and should thus allow a confident assignment of the observed absorptions.

There are four IR-active vibrations for $C_7H_7^+$, with symmetries $A_2'' + 3\ E_1'$. It was the identification of these four infrared modes which, in part, allowed the identification of the tropyl cation in the first instance.[10] The assigned vibrational frequencies had values of 633, 992, 1477, and 3020 cm^{-1}, although another relatively strong IR band was observed at 658 cm^{-1}, together with some weaker features. When compared with the calculated IR-active vibrations in Table 1, it may be seen that the corresponding MP2/6-311G(2d,p) values are 656.5, 1005.4, 1623.1, and 3202.7 cm^{-1}, whereas the B3LYP/cc-pVTZ values are 663.3, 1012.4, 1554.7, and 3183.8 cm^{-1}. It is not clear whether the 633 cm^{-1} or the 658 cm^{-1} corresponds to the calculated frequency of ca. 660 cm^{-1} (ω_4), but it *is* clear that there is only one IR-active mode calculated in this region, and so the other feature must be due to an overtone or combination band or gain intensity via some other mechanism (vide infra). Thus reasonable agreement is obtained with the experimental frequencies and also the calculated infrared intensity pattern. The agreement is not perfect, however, and this may be attributed to a number of facts: (i) the calculated values are harmonic values, as opposed to vibrational separations; (ii) the experimental values have been recorded in solution (or in inorganic compounds in some experiments, vide infra), and so are prone to perturbation, especially since a counteranion is probably in close proximity; (iii) the calculations are not performed with infinite basis sets, nor do they include all the electron correlation energy. Despite these deficiencies in the comparison of experiment and theory, it seems clear that the assignment of the four IR-active bands is unambiguous.

A suggestion for the observation of the intense IR feature at 658 cm^{-1} is given in ref 10; the same feature may also have been seen by Sourisseau and Hervieu[5] at 648 cm^{-1}. The latter authors suggested an assignment of this feature to an E_3'' mode (but they also suggested an alternative assignment of this feature to the A_2'' mode), but, as pointed out by Garbuzova et al.,[27] the assignment to a mode of E_3'' symmetry is inconsistent with its strong intensity in the IR spectrum. They[27] suggest that the band may be assigned as a combination band: $\omega_{12} + 220$ cm^{-1}.

TABLE 3: Calculated Geometric Parameters and Harmonic Vibrational Frequencies for *c*-C_7H_7 ($^2B_1$)

quantity[a]	UHF/6-31G**	ROHF/6-31G**	UMP2/6-31G**	UB3LYP/6-31G**	CASSCF(5,5)/6-31G**	CASSCF(7,7)/6-31G**
energy/E_h	−269.112489	−269.08771	−269.99792	−270.89307	−269.14842	−269.180057
r_1/Å	1.4159	1.4179	1.4126	1.4162	1.4218	1.4209
r_2/Å	1.3769	1.3528	1.3535	1.3772	1.3718	1.3731
r_3/Å	1.4660	1.4510	1.4393	1.4496	1.4653	1.4600
r_4/Å	1.3316	1.3396	1.3711	1.3607	1.3314	1.3550
s_1/Å	1.0762	1.0745	1.0812	1.0859	1.0752	1.0754
s_2/Å	1.0781	1.0783	1.0860	1.0898	1.0779	1.0780
s_3/Å	1.0762	1.0762	1.0828	1.0867	1.0760	1.0760
s_4/Å	1.0774	1.0773	1.0849	1.0885	1.0774	1.0772
ω_1 (a_1)	440.5	447.4	421.9	419.3	441.3	441.5
ω_2	856.3	864.9	861.3	845.3	886.5	865.6
ω_3	975.2	981.9	934.3	913.8	976.1	974.8
ω_4	1007.0	994.6	994.8	973.4	999.3	994.6
ω_5	1294.7	1326.9	1273.9	1248.4	1316.3	1306.5
ω_6	1382.4	1378.7	1316.4	1289.7	1383.2	1371.7
ω_7	1589.1	1596.1	1523.1	1489.2	1589.0	1589.0
ω_8	1657.5	1637.8	1620.0	1614.0	1689.9	1682.7
ω_9	1852.3	1826.5	1720.3	1666.1	1850.8	1754.2
ω_{10}	3307.4	3311.3	3236.2	3144.1	3309.3	3308.2
ω_{11}	3329.2	3333.5	3251.9	3168.5	3331.5	3329.0
ω_{12}	3342.3	3351.4	3274.8	3185.6	3348.0	3345.5
ω_{13}	3354.0	3363.9	3290.1	3191.9	3358.2	3356.4
ω_{14} (a_2)	299.0	319.5	294.4	289.3	302.2	294.4
ω_{15}	569.2	627.4	554.1	566.6	583.7	600.0
ω_{16}	781.4	869.6	829.4	768.9	762.6	763.7
ω_{17}	1019.6	1123.3	939.6	994.0	997.9	995.0
ω_{18}	1128.2	1133.4	1085.3	1009.3	1128.1	1004.3
ω_{19} (b_1)	150.1	162.9	141.5	160.2	150.5	165.5
ω_{20}	528.8	561.3	495.0	516.6	515.5	521.2
ω_{21}	669.3	688.7	675.9	656.6	655.0	657.4
ω_{22}	811.0	821.6	750.2	758.5	798.9	756.0
ω_{23}	886.8	946.6	868.4	845.3	875.2	882.7
ω_{24}	1013.8	1110.7	1037.2	985.2	988.0	989.9
ω_{25} (b_2)	468.9	476.4	452.7	446.1	469.1	446.7
ω_{26}	967.9	951.6	906.2	905.2	958.1	970.0
ω_{27}	987.5	964.7	985.7	973.4	996.4	998.4
ω_{28}	1244.7	1066.5	1199.3	1193.6	1062.4	1245.3
ω_{29}	1395.1	1307.3	1335.7	1307.8	1266.5	1405.9
ω_{30}	1524.7	1425.8	1446.8	1418.9	1422.4	1525.4
ω_{31}	1579.8	1533.2	1484.2	1485.6	1526.2	1589.7
ω_{32}	1621.0	1607.9	1574.5	1561.4	1591.9	1661.0
ω_{33}[b]	*5803.5*	*1711.9*	*4595.9*	*24.1*	*1671.0*	*98.7*
ω_{34}	3303.7	3309.7	3221.5	3144.6	3309.5	3307.6
ω_{35}	3312.1	3319.1	3237.6	3151.3	3317.3	3315.9
ω_{36}	3342.1	3347.4	3272.8	3183.3	3345.4	3344.1

[a] r_{1-4} are C−C bond lengths, running consecutively; r_4 is bisected by the C_2 axis. s_{1-4} are C−H bond lengths, running consecutively; the C_2 axis is coincident with s_1. Other distances are found directly by consideration of the C_{2v} symmetry of the molecule. [b] The italicized vibrational frequencies of b_2 symmetry (ω_{33}) have unrealistic values; see text for details.

This assignment explains the IR activity of this combination band, perhaps via a Fermi resonance with the allowed ω_4 vibration, but only if the 220 cm^{-1} vibration is not of E_3'' symmetry, as suggested by Howard and Graham, but of E_2'' symmetry. We are unable to distinguish between these two possibilities from the normal coordinate analysis, but if the authors of ref 27 are correct, then the 220 cm^{-1} vibration is ω_{14} (E_2'') in order to make the Fermi resonance proposal viable.

A weak IR feature at 353 cm^{-1} was also observed in ref 5, but was not observed in ref 27. From Table 1 it may be seen that there are no vibrations that can be associated with this value: fundamentals, combinations, or overtones. Consequently, we concur with the authors of ref 27 that the feature seen in ref 5 cannot be associated with the tropyl cation.

(ii) Raman-Active Modes. Again, the presence of a low number of Raman-active vibrations comprised part of the evidence for the identification of $C_7H_7^+$ (ref 10). Simple group theory again allows the symmetry of these modes to be determined as $2A_1' + E_1'' + 4E_2'$. Fateley et al. (ref 10) obtained Raman shifts of 433, 868, 925, 1210, 1594, 3045, and 3085 cm^{-1}, which may be compared with the calculated values of 429.6, 869.3, 912.2, 1248.9, 1688.2, 3193.0 and 3207.5 cm^{-1} at the MP2/6-311G(2d,p) level of theory, 440.7, 878.0, 903.8, 1254.7, 1631.0, 3174.0 and 3189.0 cm^{-1} at the B3LYP/cc-pVTZ level, where again good agreement may be seen. The symmetries of these assignments also match those assigned in ref 10, and additionally, the good agreement with the calculated Raman intensity pattern gives added confidence to the assignment of these vibrations.

(iii) Infrared- and Raman-Inactive Vibrations. The assignment of the sets of IR-active and Raman-active vibrations is quite straightforward, despite the fact that the calculations were performed in C_s symmetry, yielding vibrational symmetry assignments of A′ and A″ only. Thus, out of the 20 vibrational frequencies, 11 have been assigned, leaving the 9 inactive modes. Of course, these were not seen in ref 10, since the tropylium cation was in an isotropic environment; however, the studies on inorganic salts[5,6,27] had the advantage that the effective symmetry is lowered from D_{7h}, and so many more of the vibrational modes become active. Naturally, now there is the

problem that the vibrational frequencies of $C_7H_7^+$ have been perturbed by the presence of the moieties that are lowering the symmetry, but nevertheless, it may be hoped that these perturbations are small. Sourisseau and Hervieu[5] and Howard and Graham[6] present fairly complete analyses of the vibrational spectrum; however, each are not complete, with some of the assignments of the former having been questioned in ref 27.

Sourisseau and Hervieu obtained IR and Raman spectra of a number of inorganic salts in both solution and in the solid state, between 30 and 4000 cm^{-1}. This allowed a fairly complete assignment of the vibrational modes to be proposed, although it was not possible to do this unambiguously. In particular, it was not possible uniquely to associate 648 and 1025 cm^{-1} vibrations with a particular symmetry class. In addition, as mentioned above, an absorption at 353 cm^{-1} was assigned as an E_2'' fundamental mode, but this absorption was not observed in ref 27, nor is it consistent with the calculated values in Table 1. There are further assignments in ref 5, which do not concur with the calculated values; these are all associated with vibrations that are forbidden in IR and Raman spectroscopies. Specifically the assignments of ν_{14} (353 cm^{-1}), ν_{17} (1100 cm^{-1}), and ν_{18} (768 cm^{-1}) and the tentative assignment of ν_{20} (648 cm^{-1}) seem dubious.

Howard and Graham[6] used the technique of incoherent inelastic neutron scattering (IINS) as well as far-IR studies to study tropyl-cation-containing inorganic compounds. IINS has the advantage that it is not subject to dipole selection rules. In this way, it was possible to assign a number of the low-frequency modes. Their assignments were as follows: ν_2 (879 cm^{-1}), ν_{18} (776 cm^{-1}), ν_4 (~680 cm^{-1}), ν_{13} or ν_{19} (562 cm^{-1}), ν_{12} (~438 cm^{-1}) ν_{14} (~335 cm^{-1}), and ν_{20} (238 cm^{-1}). (It should be noted that these are only representative numbers, as the measured values in ref 6 varied slightly with technique and temperature.) Comparison with the calculate values in Table 1 show that ν_2, ν_4, ν_{12}, and ν_{20} are probably reasonable assignments; however, ν_{18} seems to be in error, as does ν_{14}. The 562 cm^{-1} absorption cannot be numbered unambiguously here, but the calculated frequency of 566.9 cm^{-1} (B3LYP/cc-pVTZ) is in good agreement, and so we conclude that it is either ω_{13} (E_2'') or ω_{19} (E_3'').

Unfortunately, although some of the previously suggested assignments could be ruled out, it was not possible to assign all of the vibrations here; however, the calculated values in Table 1 should provide a valuable reference point for future experimental and theoretical efforts in this area.

(iv) Comparison with the REMPI Results of Reference 11. As mentioned in the Introduction, Koenig and Chang[12] recorded a HeI PES spectrum of the tropyl radical, formed by the pyrolysis of bitropyl at 400 °C. Some vibrational structure was seen in the first band of the radical, which ought to correspond to that of the ground-state tropyl cation. The vibrational spacings observed were reported as 1424 ± 100 cm^{-1}, which were associated with the ω_6 mode (the nomenclature of the modes used here follows that of Table 2), which was observed by Fateley et al. (ref 10) at 1477 cm^{-1} and has E_1' symmetry. As was noted by Johnson,[11] if D_{7h} symmetry is present in both the neutral and cation, then this mode should only appear as double quanta in the PES spectrum. Additionally, Johnson saw vibrational spacings of 862, 1284, and 1528 cm^{-1} in his REMPI study. The first he assigned as the ω_2 mode (A_1' symmetry), which would be allowed in single quanta (assuming the Rydberg state and the neutral have D_{7h} symmetry); the second two frequencies were assigned as being double quanta excitations, giving assignments to two modes of 642 and 764 cm^{-1}, respectively. Inspection of Table 1 suggests that the assignment of ω_2 is reasonable, although an assignment to double quanta of ω_{12} (C−C stretch) would also be plausible. The assignment of the 642 cm^{-1} vibration to ω_4 (an out-of-plane deformation) also seems reasonable, although Johnson assigns this a symmetry of E_3'', which would make the assignment to ω_{13} possible; on the other hand, the 764 cm^{-1} assignment is less clear. Johnson assigns this to a ring bending mode of E_3' symmetry, but the lowest vibrational frequency of E_3' symmetry is ω_{18} at ca 900 cm^{-1}, from Table 1. There appear to be no candidates for this assignment.

TABLE 4: Declension of Symmetry from D_{7h} to C_{2v}[a]

D_{7h}	C_{2v}
A_1'	A_1
A_1''	B_2
A_2'	A_2
A_2''	B_1
E_1'	$A_1 \oplus B_2$
E_1''	$A_2 \oplus B_1$
E_2'	$A_1 \oplus B_2$
E_2''	$A_2 \oplus B_1$
E_3'	$A_1 \oplus B_2$
E_3''	$A_2 \oplus B_1$

[a] Where for the D_{7h} point group, the z-axis is the C_7-axis, and for the C_{2v} point group, the z-axis is the C_2-axis, with the molecule lying in the yz-plane.

It is noteworthy that Johnson's fundamental frequencies are based on the D_{7h} selection rules holding, but as noted above, the tropyl radical is subject to a Jahn−Teller distortion, and although the indications are that this distortion is small, it may be enough to allow the C_{2v} point group to be more applicable when deriving the selection rules; additionally, the calculated equilibrium geometry of the neutral is of C_{2v} symmetry (vide supra). Thus, it might be possible to assign the 1284 cm^{-1} progression to single quanta of a vibration, possibly ω_{17}; also the 1528 cm^{-1} progression could then be assigned to ω_6 or ω_{16}. Since these have E_1' or E_3' symmetry, each of which has a totally symmetric component in the C_{2v} point group (see Table 4). It thus seems clear that the assignment of the HeI PES and REMPI spectra are far from definitive and that higher-resolution MPI and photoelectron experiments would be useful. We note in passing that the high-resolution zero-kinetic-energy (ZEKE) PES of the benzyl radical (a C_7H_7 isomer) has been reported.[28]

c. Vibrational Frequencies of c-C_7H_7. To the authors' knowledge no vibrational frequencies of the tropyl radical have been reported. To this end, calculated values are presented in Table 3. As noted in the Theoretical Methods section, there were difficulties in the use of unrestricted wave functions, since these have significant spin contamination. Although the geometry appeared to be rather insensitive to this, the vibrational frequencies seemed more so, as indicated by some very large and some very small values of ω_{33}. It is noteworthy that the vibrational modes that appear to have a problem with spin-contamination are localized to those of b_2 symmetry. The anomalously high values of the vibrational frequencies are not present when restricted methods are used (ROHF) or when the spin-contamination is smaller (UB3LYP/6-31G**); however, there is a problem with anomalously *low* values of the ω_{33} vibrational mode in the latter calculations. CASSCF calculations were then performed, which are restricted, and so will also not suffer from spin contamination. As may be seen, the CASSCF(5,5) calculations led to values for the vibrational frequencies that were very similar to those from the ROHF calculations; however, CASSCF(7,7) calculations, in which all the outermost π electrons are included, lead to a low value again,

TABLE 5: Calculated Electronic Excitation Energies for c-$C_7H_7^+$ at the CIS/6-311++G//MP2/6-31G** Level**

state no.	spin multiplicity[a]	symmetry[a]	energy/eV	λ/nm	oscillator strength
1	T	E	3.1	394	0
2	T	E	3.9	320	0
3	S	E	5.1	242	0
4	T	E	6.2	201	0
5	T	A	7.1	174	0
6	S	E	7.3	170	1.28
7	T	E	7.5	166	0
8	S	A	7.7	160	0.01

[a] Where T represent a triplet state and S represents a singlet state. E means the state is doubly degenerate, and A means the state is singly degenerate.

TABLE 6: Calculated AIE and VIE for the c-C_7H_7 Radical at the MP2/6-31G Optimized Geometry (eV)**

method	AIE (+ZPVE)[a]	VIE
MP2/6-31G**	5.26 (5.38)	5.45
MP2/6-31G(2d,p)		5.51
CCSD/6-31G(2d,p)		5.76
B3LYP/6-31G(2d,p)	5.80 (5.92)	5.80
B3LYP/6-311G(3df,2p)	5.92 (6.04)	6.07
B3LYP/cc-pVTZ	5.94 (6.06)	6.09
B3LYP/cc-pVQZ	5.97 (6.09)	6.12
experimental	6.24[b]/6.28[c]	6.28[c]

[a] The ZPVE has been calculated by use of the RHF vibrational frequencies for the cation, and the ROHF vibrational frequencies for the neutral (taking account of degeneracies), each scaled by 0.89. [b] References 14 and 17. [c] References 12.

more akin to the UB3LYP calculations. Since there are no experimental values available, we say nothing more on these values, except to comment that this particular b_2 (ω_{33}) mode seems to be extremely sensitive to the level of calculation. Despite the large variation in the magnitude of this computed harmonic frequency, it seems to be essentially the same normal mode but with very different contributions from the carbon skeletal and the C−H wagging motions. The former leads to a small vibrational frequency and the latter a large vibrational frequency; nevertheless, apart from this mode, the computed results for the harmonic vibrational frequencies at all levels are very consistent.

d. Excited Electronic States. The results of the CIS/6-311++G** calculations are shown in Table 5. As may be seen, there are singlet states at 5.1 eV, which corresponds to a wavelength of ca. 242 nm, which is in very good agreement with the spectrum seen by von E. Doering and Knox[8] (247−275 nm). In addition, this value is not inconsistent with value of 4.33 eV (286 nm) calculated by Murrell and Longuet-Higgens,[18] but in much better agreement with the value of 5.3 eV calculated by Gallup and Norbeck,[19] who indicate that it is of E_3 symmetry. The oscillator strength of this transition (Table 5) is predicted to be zero, however, in line with the forbidden nature of this transition, but this may become allowed through vibronic coupling, or solvent effects, explaining its observation in ref 8. The results also indicate that there are two triplet states at 3.1 and 3.9 eV, which are slightly lower than the 4.3 eV calculated for both states by Gallup and Norbeck,[19] but the lowest is consistent with the state tentatively assigned by Koenig and Chang in their PES study.[12] The inference of a state at 0.51 eV by Elder and Parr[17] is not supported by the calculations reported either here or in ref 19 and is probably an artifact.

e. Ionization Energy of c-C_7H_7. The calculated ionization energies are given in Table 6. All of these values were obtained from single-point energy calculations at the MP2/6-31G** optimized geometries of the neutral and cation. The ZPVE correction was only made to the AIE, since for the VIE the precise correction is not clear, but it ought to be much smaller than that for the AIE. Thus, the AIE and VIE are almost coincident, in agreement with the HeI PES study.[12] As may be seen, these values are in good agreement with the value of 6.28 eV obtained in the HeI photoelectron study,[12] which was the energy of the first vibrational component of the first band of the tropyl radical (which appears to be the vertical component). The value obtained from photoionization efficiency (PIE) measurements (6.236 ± 0.005 eV)[17] and that obtained from Rydberg extrapolation (6.237 eV)[14] suggest that in fact the calculated values may be in error by 0.13 eV. The values in Table 6 show that the AIE has not converged with basis set, and this is the probably the major source of error in the present calculations. [The good agreement between the B3LYP/6-31G-(2d,p) and CCSD/6-31G(2d,p) values for the VIE suggest that electron correlation energy is not the problem here.] Clearly, for such a large molecule, calculations with larger basis sets are going to be expensive (for the cc-pVQZ basis set, there are 595 basis functions for the tropyl cation and neutral). Of course, the experimental values may also be prone to some error: PIE measurements may well not see the true onset, and the Rydberg extrapolation of ref 14 was based on rather a small number of components. All things considered, the agreement is pleasing.

After this paper had been completed, a recent paper by Smith and Hall[29] was discovered, in which G2 (MP2, SVP)[30] were performed on the tropyl radical and cation. An ionization energy of 6.19 eV was obtained, which is in very good agreement with the value of 6.09 eV obtained in the present work.

It is perhaps worth noting in passing that a very recent paper on cycloheptatrienyl sandwich compounds with actinides[31] contains a D_{7h} point group character table.

V. Conclusions

Ab initio molecular orbital and density functional theory (DFT) calculations have been performed on the tropyl cation (c-$C_7H_7^+$) and the tropyl radical (c-C_7H_7). The results indicate that the tropyl cation has a D_{7h} geometry, in agreement with previous experimental results, with the radical having a C_{2v} geometry, which is not wholly consistent with the results of ESR studies.

Vibrational harmonic frequencies were calculated for the cation and the neutral. For the neutral there was no experimental evidence to which to compare. For the cation there are a number of experimental studies, but the assignments presented in those studies have inconsistencies. To a large extent these inconsistencies have been clarified, but the complete assignment of the vibrational modes of the tropyl cation has not yet been achieved.

The excited states of the tropyl cation were studied at the CIS/6-311++G** level, and these were basically in agreement with previous theoretical results and the small amount of experimental data; however, the suggestion of an excited state at 0.51 eV from a PIE study was able to be excluded.

Finally the AIE and VIE of the first band of the tropyl radical were calculated and found to be in very good agreement with experimental determinations; suggestions for the remaining discrepancies were made.

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