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Vibrational Spectra of Butatriene (C_4H_4) and Pentatetraene (C_5H_4): Is Pentatetraene Bent?

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Abstract: The vibrational spectra of butatriene (C_4H_4) and pentatetraene (C_5H_4) are predicted with use of the configuration interaction method and double-ζ (DZ) basis sets with/without polarization functions. The experimental assignment for most of the vibrations of C_4H_4 agrees with the present theoretical predictions for the linear structure, but some tentative Raman assignments (for CH_2 rocking, wagging, and the b_{2g} CCC bending) seem to be questionable since they differ from the best theoretical evaluations by as much as 60%. The vibrational spectrum of C_5H_4 is completely characterized for the first time, and it is found that there are large discrepancies between most of the experimentally assigned IR bands and the present theoretical frequencies obtained for the linear structure. It is also shown that the CCC bending frequencies in C_4H_4 and C_5H_4 are extremely sensitive to basis set and electron correlation method. Thus, the DZ, 6-31G, and triple-ζ (TZ) basis sets, when used in conjunction with methods explicitly incorporating the effects of electron correlation, give quite different predictions of the vibrational frequencies for CCC bending in these molecules. The second-order Møller–Plesent perturbation and the single and double configuration interaction methods are also significantly different in this respect. All theoretical methods except TZ MP2 and those involving the 6-31G basis set predict that the carbon skeleton of pentatetraene is linear. However, it is concluded that more experimental studies of C_5H_4 are necessary to characterize the structure for its ground electronic state.

1. Introduction

In an attempt to give a unified explanation of the double bond deformation of both ethylene analogues and cumulenones, Trinquier and Malrieu[1] proposed an important model based on valence bond theory. They assume that the fragments forming a double bond tend to preserve their "individualities" when possible. For example, when two XH_2 fragments form $H_2X{=}XH_2$, two dative bonds will be created from the singlet states of the fragments if those singlet states are much more stable than their triplet states (for instance for SiH_2), and the resulting molecule will be trans-bent. This model attributes the deformation of double bonds to essentially two local properties of the molecule: the strength of the double bond and the singlet–triplet energy separation of the fragments forming this bond.[1] More specifically, the work of Trinquier and Malrieu is grounded on the presumption that the longer the cumulene carbene, the less easy the CCC bending. Trinquier and Malrieu also discussed the effects of electron correlation on the trans bending vibrational frequencies of these systems.

Although this conceptually simple and appealing model has been successfully applied to many cases, it was recently discussed further by Liang and Allen.[2] They claim that whether a double bond distorts or not depends on the property of the entire molecule, especially in cases where the double bond in question is part of an extensively electron delocalized structure. They proposed an alternative model based on the second-order Jahn–Teller theory to explain the known double bond deformations.[2] They further predicted that longer cumulenes (such as pentatetraene), rather than shorter ones (such as butatriene) as Trinquier and Malrieu expected,[1] should be bent. However, Liang and Allen's prediction was confirmed with only a moderate theoretical method, namely Møller–Plesent second-order perturbation (MP2) theory with the 6-31G basis set.[2] Therefore, we decided to carry out a more rigorous theoretical study on these two crucial molecules, namely butatriene (C_4H_4) and pentatetraene (C_5H_4), to test the above two theories concerning double bond deformation. Butatriene was synthesized[3] in 1954 and has been characterized with use of Raman,[4] IR,[5] UV,[6] and electron diffraction[7] methods. Many substituted butatrienes are also known.[8-14] Pentatetraene was synthesized[15] much later because of its reactivity and only a few IR absorptions were reported, with most of them unassigned.[16] There are also fewer substituted pentatetraenes (than butatrienes) reported.[14,17-20] Pentatetraene remains to be characterized in any detail experimentally.

There are many ab initio, as well as experimental, studies on the bending of cumulated double bonds. Examples are propadienone,[21] butatrienone,[22] carbon suboxide,[23] diazoethene,[24] and

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Table I. Theoretical Geometrical Parameters of Butatriene and Pentatetraene[a]

	C_4H_4				C_5H_4			
method	C_1–C_2	C_1–C_3	C–H	HCH	C_1–C_2	C_2–C_4	C–H	HCH
DZ SCF	1.273	1.316	1.075	117.3	1.277	1.312	1.075	117.5
DZ+d SCF	1.270	1.311	1.077	118.0	1.275	1.307	1.077	118.3
DZP SCF	1.269	1.310	1.078	118.2	1.275	1.306	1.078	118.5
DZ CISD	1.291	1.338	1.089	177.3	1.294	1.332	1.089	117.4
DZ+d CISD	1.279	1.323	1.085	118.1	1.283	1.317	1.084	118.3
DZP CISD	1.278	1.322	1.083	118.2	1.283	1.316	1.082	118.5

[a] Bond lengths in Å and angles in deg.

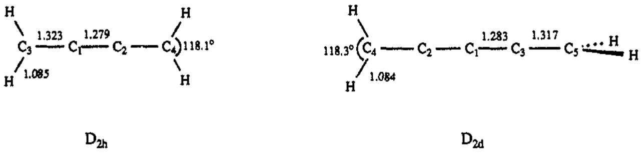

Figure 1. The DZ+d CISD predicted geometries for butatriene (C_4H_4) and pentatetraene (C_5H_4). Bond distances are in Å.

difluoropropadienone.[25] However, no one except Liang and Allen[2] has theoretically studied the bending of cumulenes, even though they are isoelectronic with the above molecules. Other ab initio studies on butatriene and pentatetraene were limited to the self-consistent-field (SCF) method with minimum[26] or split valence basis sets[6] and were performed for interpreting the UV spectra of these molecules. Therefore, relatively little is known about butatriene apart from early experimental studies and even less is known about pentatetraene. This paper presents the first ab initio study of the structure and vibrational spectra of these two molecules using high level theoretical methods.

2. Theoretical Methods

The SCF and CISD (configuration interaction including all single and double excitations from the reference Hartree–Fock determinant) methods have been employed to study the equilibrium geometry and vibrational spectra of butatriene (with D_{2h} symmetry) and pentatetraene (with D_{2d} symmetry) (Figure 1). Both SCF and CISD energy gradients are evaluated analytically with methods developed in this group.[27-29] The SCF force constants are also evaluated with analytic methods,[30,31] but a seminumerical method, which uses finite displacements from the equilibrium geometry in conjunction with analytic gradient evaluations, is employed to obtain the CISD force constants. The internal coordinates are defined according to Pulay, Fogarasi, Pang, and Boggs' recommendations.[32] For butatriene, 22 completely symmetrized displacements are required to generate the full force constant matrix. For pentatetraene, 10 symmetrized displacements are needed for the torsion, C–C stretchings, and CH_2 scissorings, and 7 simple displacements with C_s symmetry are used for the other vibrations. Harmonic vibrational frequencies are determined from the force constant matrices in the standard manner.[33] The potential energy distribution (PED) of each normal mode is deter-

Table II. SCF Predicted IR Spectra of Butatriene (D_{2h})[a]

	frequency			IR intensity	assignment
sym	DZ	DZ+d	DZP	DZ+d	DZ+d
a_g	3326	3333	3310		CH str (99)
	2378	2340	2341		C_1C_2 str (57) + C_1C_3 str (42)
	1612	1598	1586		CH_2 sciss (94)
	945	952	953		C_1C_3 str (57) + C_1C_2 str (40)
a_u	842	828	825		CH_2 twist (100)
b_{1g}	3427	3428	3402		CH str (100)
	1144	1106	1108		CH_2 rock (96) + CCC bend (4)
	426	371	371		CCC bend (90) + CH_2 rock (10)
b_{1u}	1076	1016	1012	119	CH_2 wag (99)
	255	240	241	10	CCC bend (100)
b_{2g}	1075	1014	1009		CH_2 wag (98)
	646	603	603		CCC bend (99)
b_{2u}	3427	3429	3403	11	CH str (100)
	1157	1127	1127	1	CH_2 rock (98)
	248	238	238	11	CCC bend (89) + CH_2 rock (11)
b_{3u}	3327	3335	3312	14	CH str (99)
	1794	1804	1800	33	C_1C_3 str (80) + CH_2 sciss (19)
	1544	1518	1509	1	CH_2 sciss (86) + C_1C_3 str (14)

[a] Harmonic vibrational frequencies are given in cm^{-1} and IR intensities in km/mol. The assignments are based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix of butatriene. Data in parentheses are percentage contributions.

Table III. Experimental and CISD Predicted Vibrational Spectra of Butatriene (D_{2h})[a]

	frequency			IR intensity		assignment
sym	DZ	DZ+d	exp[b]	DZ+d	exp[b]	DZ+d
a_g	3183	3242	2995			CH str (99)
	2229	2255	2079			C_1C_2 str (57) + C_1C_3 str (42)
	1535	1532	1430			CH_2 sciss (94)
	892	919	878			C_1C_3 str (57) + C_1C_2 str (40)
a_u	787	792	736[c]		w	CH_2 twist (100)
b_{1g}	3280	3342	3059			CH str (100)
	1066	1045	663			CH_2 rock (97)
	333	295	234[c]			CCC bend (91) + CH_2 rock (9)
b_{1u}	915	896	854	121	vs	CH_2 wag (99)
	226	223	(?)[c]	7		CCC bend (99)
b_{2g}	913	894	544			CH_2 wag (99)
	552	539	330[c]			CCC bend (96)
b_{2u}	3280	3342	3080[d]	7	m	CH str (100)
	1092	1076	1060[d]	0	w	CH_2 rock (98)
	221	217	215[c]	10	vs	CCC bend (88) + CH_2 rock (12)
b_{3u}	3182	3242	2994	6	m	CH str (99)
	1685	1733	1608[c]	18	s	C_1C_3 str (82) + CH_2 sciss (18)
	1472	1461	1370	0	w	CH_2 sciss (87) + C_1C_3 str (12)

[a] Harmonic vibrational frequencies are given in cm^{-1} and theoretical IR intensities in km/mol. The assignments are based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix of butatriene. Data in parentheses are percentage contributions. [b] Experimental data are from: Miller, F. A.; Matsubara, I. *Spectrochim. Acta* **1966**, *22*, 173. Note that Herzberg's convention for irreducible representations is used here. [c] Uncertain assignments. [d] Large error bar (±20 cm^{-1}).

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Table IV. SCF Predicted IR Spectra of Pentatetraene (D_{2d})[a]

	frequency			IR intensity	assignment
sym	DZ	DZ+d	DZP	DZ+d	DZ+d
a_1	3324	3332	3310		CH str (99)
	2084	2075	2075		C_2C_4 str (65) + C_1C_2 str (32)
	1584	1564	1551		CH_2 sciss (96)
	787	794	794		C_1C_2 str (65) + C_2C_4 str (34)
b_1	757	743	740		CH_2 twist (100)
b_2	3323	3330	3309	8	CH str (99)
	2424	2375	2375	323	C_1C_2 str (78) + C_2C_4 str (22)
	1644	1645	1635	10	CH_2 sciss (62) + C_2C_4 str (31)
	1420	1409	1406	22	C_2C_4 str (50) + CH_2 sciss (38)
e	3425	3426	3402	2	CH str (100)
	1136	1100	1100	0	CH_2 rock (95)
	1054	991	986	67	CH_2 wag (97)
	626	561	562	1	$C_1C_2C_4$ bend (64) + $C_2C_1C_3$ bend (36)
	392	357	360	0	$C_1C_2C_4$ bend (77) + $C_2C_1C_3$ bend (15)
	169	159	160	7	$C_2C_1C_3$ bend (59) + $C_1C_2C_4$ bend (37)

[a] Harmonic vibrational frequencies are given in cm^{-1} and IR intensities in km/mol. The assignments are based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix of pentatetraene. Data in parentheses are percentage contributions.

mined with the INTDER program developed in this group (the totally symmetrized internal coordinates are used here).

Three basis sets are employed in this study: (a) Huzinaga–Dunning's double-ζ basis set (DZ, 9s5p/4s2p on carbon and 4s/2s on hydrogen; a scale factor of 1.2 was applied to the exponents of the hydrogen primitives);[34] (b) Huzinaga–Dunning's DZ basis set augmented by a set of six d-like functions ($\alpha_d = 0.75$) on carbon (DZ+d); and (c) DZ+d basis set plus polarization (hydrogen $\alpha_p = 0.75$) basis set (DZP). The carbon 1s-like orbitals and the corresponding virtual orbitals are frozen/deleted from all CISD wave functions. Thus, there are 20 515 and 70 003 configurations in the DZ+d (CISD wave functions for the D_{2h} symmetry butatriene and the D_2 symmetry pentatetraene, respectively (D_{2d} was not used for pentatetraene because of program limitations). In the CI displacement gradient evaluations for C_4H_4, the lowest symmetry considered is C_2 and its DZ+d CISD wave function contains 73 441 configurations. For C_5H_4, the wave function with lowest symmetry (C_s) has 164 749 configurations.

The optimized geometries are reported in Table I. The harmonic vibrational frequencies of butatriene are given in Tables II and III, and those of pentatetraene are listed in Tables IV and V. Table III also shows the experimental assignment[5] of the vibrational spectra for butatriene. Note that all of the vibrational frequencies predicted by the SCF method for both linear molecules in conjunction with the DZ, DZ+d, and DZP basis sets and by the CISD method in conjunction with the DZ and DZ+d basis sets are real, in disagreement with Liang and Allen's 6-31G MP2 study.[2]

3. Results

In this section, theoretical results shall be compared first. The best of these are then compared with available experimental data. We shall also discuss the CISD results obtained with Huzinaga–Dunning's basis sets with those from second-order perturbation theory and Pople's 6-31G basis set. Finally, results obtained with Huzinaga–Dunning's triple-ζ (TZ) basis set shall be presented. Further discussions on a few key issues shall be delayed until the next section.

3.1. Geometry. Three general observations may be made regarding the theoretical geometries in Table I. As is expected for hydrocarbons, electron correlation increases bond lengths slightly. Thus, the CISD predicted bond lengths are about 0.01–0.02 Å longer than the SCF predictions for the DZ basis set. But this increase in bond distances is smaller (about 0.01 Å) for the better basis sets, DZ+d and DZP. Electron correlation does not seem to have a significant effect on the theoretical bond angles (Table I). Another well-known trend is also reflected in Table I. That is, adding polarization functions shortens bond lengths. Specifically, in going from the DZ basis to the DZ+d and DZP basis sets the predicted bond lengths become about 0.005 and 0.015 Å shorter with use of the SCF and CISD methods, respectively. Finally, it is encouraging that the geometries predicted with the DZ+d basis and the DZP basis are essentially the same for both the SCF and CISD methods. This suggests that the polarization functions on hydrogens are not very important for the geometries of butatriene and pentatetraene.

Table V. CISD Predicted IR Spectra of Pentatetraene (D_{2d})[a]

	frequency		IR intensity	assignment
sym	DZ	DZ+d	DZ+d	DZ+d
a_1	3194	3251		CH str (99)
	1972	2011		C_2C_4 str (65) + C_1C_2 str (33)
	1520	1507		CH_2 sciss (96)
	748	770		C_1C_2 str (65) + C_2C_4 str (34)
b_1	723	718		CH_2 twist (100)
b_2	3191	3250	1	CH str (99)
	2289	2305	198	C_1C_2 str (78) + C_2C_4 str (22)
	1567	1583	11	CH_2 str (61) + C_2C_4 str (33)
	1352	1365	10	C_2C_4 str (48) + CH_2 sciss (40)
e	3290	3350	1	CH str (100)
	1073	1048	0	CH_2 rock (94)
	925	886	69	CH_2 wag (98)
	550	505	0	$C_1C_2C_4$ bend (63) + $C_2C_1C_3$ bend (35)
	341	314	0	$C_1C_2C_4$ bend (76) + $C_2C_1C_3$ bend (18)
	156	150	6	$C_2C_1C_3$ bend (61) + $C_1C_2C_4$ bend (35)

[a] Harmonic vibrational frequencies are given in cm^{-1} and IR intensities in km/mol. The assignments are based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix of pentatetraene. Data in parentheses are percentage contributions.

The geometry of butatriene has been determined with gas-phase electron diffraction[7] and Raman[4] methods. The former method, with error limits of ±0.005 Å, showed that the C–H, C_1–C_2, and C_1–C_3 bond lengths are 1.083, 1.283, and 1.318 Å, respectively. The Raman spectrum analysis concluded that the C_1–C_2 distance is 1.284 Å if the two outer C=C bonds (C_1—C_3) are assumed to be 1.309 Å, the experimental C=C bond length in allene. But if one assumes the C_1–C_3 distance to be 1.318 Å, the distance obtained from electron diffraction,[7] the same analysis would give a C_1–C_2 distance of 1.270 Å. Apparently, there is a large uncertainty in these experimental bond lengths. However, our DZ+d (and DZP) CISD predictions (1.279 Å for C_1–C_2 and 1.323 Å for C_1–C_3) are within the range given by experiments. Assuming the C–H distance to be 1.085 Å, the ∠HCH angle was estimated to be 119 ± 0.5° from the rotational Raman measurements.[5] That angle is slightly larger than the DZ+d CISD prediction (118.1°). But the theoretical value for butatriene is very close to that found in allene (118.3 ± 0.3°).[35] The structure of pentatetraene has not been determined by experiment.

There are a few crystal structures of substituted butatrienes reported. Although the outer two C=C bond lengths in substituted butatrienes (varying from 1.319 to 1.345 Å) are close to that of the parent molecule, the central C=C bond distances are considerably shorter in most of the cases (varying from 1.246 to 1.276 Å).[8,9,12] Only two crystal structures of substituted pentatetraenes were reported so far.[14] The central C=C bond distances are found to be 1.276 and 1.271 Å, and the outer C=C bond lengths 1.315 and 1.327 Å. Again, the central bonds in substituted pentatetraenes are shorter than the DZ+d CISD estimate for the parent molecule (1.283 Å), while the outer C=C distance from theory (1.317 Å by DZ+d CISD) agrees well with those found experimentally for the substituted pentatetraenes.

3.2. Vibrational Frequencies of Butatriene. The data in Tables II and III show that polarization functions on carbon are very important in predicting the vibrational frequencies of butatriene. The differences in frequencies obtained from the DZ and DZ+d basis sets range from −0.7 to 14.8% (SCF, with an average of 3.2%) and from −2.9 to 12.9% (CISD, with an average of 2.3%). In particular, the frequencies for CCC bendings and CH_2 waggings

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obtained with the DZ basis are too high compared to those from the DZ+d basis, although the two basis sets agree on other frequencies. For instance, the DZ predicted frequency for the b_{1g} (trans) CCC bending frequency is 14.8% (SCF) and 12.9% (CISD) higher than the corresponding DZ+d predictions. These indicate that polarization functions are necessary to describe the bending of cumulated double bonds, in agreement with other ab initio studies of related systems.[22b,23]

It is encouraging to note that all of the DZP SCF vibrational frequencies differ by less than 1% from the DZ+d SCF values (Table II). The average difference is only 0.3% with the DZ+d SCF values being higher for most of the normal modes. This suggests that the polarization functions on hydrogen are not very important in predicting the SCF vibrational frequencies (it has been noted above that p-functions on hydrogen have negligible effect on geometries). Therefore, no CISD frequencies were evaluated with the DZP basis set since they may not be significantly different from the DZ+d CISD values and their evaluation would require considerably more computation.

In agreement with other theoretical studies on the bending of cumulated double bonds in other molecules,[2,21,22a,24] electron correlation has a significant effect on the theoretical vibrational frequencies (Tables II and III) of butatriene and pentatetraene. The average difference between CISD and SCF frequencies is 9.6% (range: 4.5–27.9%) for the DZ basis and 7.1% (range: 2.6–25.8%) for the DZ+d basis, the SCF values being always higher. Once again, large differences are found in the vibrational frequencies involving CCC bending and CH_2 wagging. For instance, the DZ+d SCF method predicts the b_{1g} CCC bending to be 371 cm^{-1}, which is 25.8% higher than the corresponding CISD prediction (295 cm^{-1}).

When our best theoretical harmonic vibrational frequencies (obtained from the DZ+d CISD method) are compared to the experimental assignments of Miller and Matsubara,[5] the agreement is reasonably good for all of the IR active bands and the Raman bands that were assigned with confidence (Table III). The error range is 0.9–9.3% with an average of 6.5% and the theoretical values being uniformly higher. However, the predicted frequencies are dramatically different from three Raman assignments that Miller and Matsubara were not absolutely sure about. They assigned the 663- and 544-cm^{-1} lines to CH_2 (b_{1g}) rocking and (b_{2g}) wagging, respectively, because these are the two strong, unassigned bands below 1430 cm^{-1}. However, Miller and Matsubara admitted that these frequencies are lower than expected. In fact, they are only 63.4 and 60.9% of our DZ+d CISD predictions (1045 cm^{-1} for CH_2 rock and 894 cm^{-1} for CH_2 wagging), which is far beyond the normal error range of comparable theoretical methods.[36]

Miller and Matsubara[5] assigned the 234- and 330-cm^{-1} bands to CCC bendings with no explanation and placed the former in b_{1g} and the latter in b_{2g} symmetry (but they switched these two in their Table 4). Though the ordering and the b_{1g} assignment agree with the present study, the b_{2g} assignment is also in unsettling disagreement with our best results: the b_{2g} CCC bending frequency of 330 cm^{-1} is only 61.2% of the DZ+d CISD prediction (539 cm^{-1}, Table III). Therefore, Miller and Matsubara's rather tentative assignments of the 663-, 544-, and 330-cm^{-1} Raman bands seem to be problematical, although their assignments of other vibrations (including the ones for CCC bending, CH_2 rocking, and wagging) appear to agree with this ab initio study. Further discussion is presented in section 4.

There are a few assignments stated as uncertain in Miller and Matsubara's IR spectrum analysis. For example, the b_{3u} symmetric C–C stretch could be either 1608 or 1711 cm^{-1} and the former was chosen because it is more intense.[5] Although both frequencies are in plausible agreement with the DZ+d CISD evaluation (1733 cm^{-1}), the theoretical IR intensity results support Miller and Matsubara's choice: the DZ+d CISD IR intensities show that 1733-cm^{-1} band should be the second strongest IR band and this corresponds to the 1608-cm^{-1} band in the solid-state IR spectrum, but not the 1711-cm^{-1} band, in spite of the fact that its frequency is closer in absolute terms to theory. Miller and Matsubara's tentative assignment of the 736-cm^{-1} band to CH_2 twisting (or torsion) seems to agree with our theoretical result (792 cm^{-1}), too.

3.3. Vibrational Frequencies of Pentatetraene. The above observations on the theoretical vibrational frequencies of butatriene are also pertinent to pentatetraene (Tables IV and V). Thus, adding d-functions on carbon to the DZ basis set reduces the CH_2 wagging and CCC bending frequencies by 5.9–10.4% at the SCF level of theory. Adding p-functions on hydrogen to the DZ+d basis set has little effect on the SCF frequencies of C_5H_4 (less than 1%). Inclusion of electron correlation once again changes the frequencies significantly. In particular, it reduces the CH_2 wagging and CCC bending frequencies by 7.7–13.0% for the DZ basis and 5.7–12.0% for the DZ+d basis set. The inconsistency of these SCF-CI changes points out the importance of an explicit treatment of correlation effects.

In the literature, six IR bands have been reported,[15,16] with two of them assigned: 3090, 2085 (C=C stretching), 1660 (C=C stretching), 1240, 1140, and 910 cm^{-1}. The assignment of the 2085-cm^{-1} band seems reasonable since it is 9.5% lower than our best theoretical estimate (2305 cm^{-1} by DZ+d CISD). It is also close to those found in substituted pentatetraenes[17–19] (2030–2060 cm^{-1}, with one exception at 1980 cm^{-1}). However, the 1660-cm^{-1} band seems too high for the other IR active C=C stretching: it is 21.6% *higher* than the nearest DZ+d CISD frequency (1365 cm^{-1}) for the motion in which C=C stretching dominates (48%, according to the PED analysis; the CH_2 scissoring contributes 40%), and it is known that theoretical vibrational frequencies are usually higher than experiment.[36] It is also 4.9% higher than the nearest DZ+d CISD frequency of any type (1583 cm^{-1}) which is dominated by CH_2 scissoring (61%, PED) and has contributions from the outer C=C bond stretching (33%, PED). On the other hand, the observed 1240-cm^{-1} band appears to agree with the theoretical value for C=C stretch (1365 cm^{-1}, by DZ+d CISD).

For the remaining three observed IR bands of C_5H_4, the one at 3090 cm^{-1} certainly belongs to the C–H stretching (it agrees with the DZ+d CISD frequencies for both IR active C–H stretchings with b_2 or e symmetry, but it is closer to the former). However, the 1140- and 910-cm^{-1} absorptions are 8.8 and 2.7% *higher* than the closest DZ+d CISD frequencies 1048 (for CH_2 rocking) and 886 cm^{-1} (for CH_2 wagging). It should be noted that the 910-cm^{-1} band seems to fit the nearest DZ CISD value of 925 cm^{-1}, while the 1140-cm^{-1} band is still higher than the nearest DZ CISD predictions (1073 cm^{-1}). Considering the fact that the DZ+d CISD level of theory successfully predicted the vibrational frequencies of butatriene, the large difference between this theoretical method and existing experiments for the analogous compound pentatetraene is puzzling and this will be discussed further in the next section.

3.4. Comparison with the 6-31G MP2 Results. As mentioned above, the SCF and CISD methods in conjunction with the Huzinaga–Dunning's DZ and DZ+d basis sets predict real vibrational frequencies for butatriene and pentatetraene. This disagrees with Liang and Allen's results[2] obtained from the 6-31G MP2 method, which predicts one imaginary frequency for each of the two cumulenes. Thus, further theoretical studies were carried out to investigate the effects of basis set and electron correlation method on the vibrational frequencies of C_4H_4 and C_5H_4. Specifically, the vibrational frequencies of these molecules were studied with the 6-31G CISD and DZ MP2 methods (MP2 geometries and vibrational frequencies are obtained with the analytic derivative methods in CADPAC[38]). The results are reported in Tables VI–VIII (the 6-31G MP2 frequencies, which were not given in ref 2, are also listed). All of the theoretical harmonic vibrational frequencies for a few key vibrations are

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(36) Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1980**, *73*, 2310.

(37) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(38) Amos, R. D.; Rice, J. E. CADPAC: The Cambridge Analytic Derivative Package, Issue 4.0, Cambridge, 1987.

Table VI. Theoretical Geometrical Parameters of Butatriene and Pentatetraene Obtained from the 6-31G Basis Set (with the SCF, MP2, CISD Methods), the DZ Basis Set (with the MP2 Method), and the TZ Basis Set (with the SCF, MP2, CISD Methods)[a]

	C_4H_4				C_5H_4			
method	C_1–C_2	C_1–C_3	C–H	HCH	C_1–C_2	C_2–C_4	C–H	HCH
6-31G SCF	1.267	1.306	1.074	116.9	1.272	1.304	1.074	117.1
6-31G MP2	1.287	1.338	1.090	116.3	1.295	1.335	1.090	116.4
6-31G CISD	1.282	1.326	1.086	116.4	1.287	1.322	1.085	116.6
DZ MP2	1.298	1.352	1.095	117.4	1.305	1.348	1.096	117.4
TZ SCF	1.262	1.304	1.075	117.0	1.268	1.302	1.075	117.3
TZ MP2	1.280	1.334	1.087	116.6	1.289	1.331	1.087	116.6
TZ CISD	1.274	1.332	1.084	116.6	1.280	1.317	1.083	116.7

[a] Bond lengths in Å and angles in deg.

Table VII. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) of Butatriene (D_{2h}) Obtained from the 6-31G Basis Set (with the SCF, MP2, CISD Methods), the DZ Basis Set (with the MP2 Method), and the TZ Basis Set (with the SCF, MP2, CISD Methods)

	6-31G			DZ	TZ		
sym	SCF	MP2	CISD	MP2	SCF	MP2	CISD
a_g	3318	3158	3201	3127	3280	3130	3172
	2411	2167	2259	2135	2351	2109	2208
	1630	1536	1559	1506	1604	1513	1552
	965	877	914	851	945	860	899
a_u	849	794	801	776	844	791	801
b_{1g}	3402	3242	3280	3229	3357	3213	3249
	1162	1072	1095	1035	1162	1090	1110
	439	216	302	286	447	263	331
b_{1u}	1081	922	973	845	1083	889	951
	238	177	191	215	238	167	188
b_{2g}	1079	916	965	844	1082	886	946
	603	286i	176	517	642	353	451
b_{2u}	3402	3242	3280	3232	3357	3214	3248
	1178	1103	1120	1070	1171	1114	1129
	250	207	219	210	247	205	218
b_{3u}	3320	3159	3201	3128	3281	3132	3172
	1826	1648	1719	1610	1780	1614	1684
	1561	1473	1494	1447	1533	1461	1484

Table VIII. Theoretical Harmonic Vibrational Frequencies (cm^{-1}) of Pentatetraene (D_{2d}) Obtained from the 6-31G Basis Set (with the SCF, MP2, CISD Methods), the DZ Basis Set (with the MP2 Method), and the TZ Basis Set (with the SCF, MP2, CISD Methods)[a]

	6-31G			DZ	TZ		
sym	SCF	MP2	CISD	MP2	SCF	MP2	CISD
a_1	3320	3157	3214	3124	3281	3218	3184
	2110	1904	1998	1873	2058	1854	1953
	1600	1512	1539	1488	1573	1507	1532
	802	729	764	709	786	715	751
b_1	762	722	732	710	758	720	732
b_2	3319	3157	3211	3123	3280	3128	3182
	2452	2194	2312	2170	2391	2131	2257
	1664	1543	1590	1515	1632	1532	1574
	1439	1323	1373	1297	1409	1297	1352
e	3403	3240	3292	3225	3356	3209	3258
	1154	1065	1094	1040	1151	1084	1110
	1058	898	963	846	1061	871	947
	581	754i	560i	516	632	177i	382
	386	237	289	311	386	305	262
	155	121	134	149	155	127	124

[a] Note that the one imaginary vibrational frequency (6-31G MP2, 6-31G CISD, and TZ MP2) in each case where it appears corresponds to the bending of the inner three-carbon atoms.

tabulated in Table IX for comparison.

First, results from the 6-31G basis set shall be compared with those from the DZ basis. Examining the data in Tables I and VI shows that 6-31G predicts shorter bond distances than does the DZ basis [by 0.010 (SCF), 0.014 (MP2), and 0.012 Å (CISD)]. The 6-31G basis set predicts ∠HCH angles that are 0.4° (SCF), 1.1° (MP2), and 0.9° (CISD) smaller than the respective DZ values (and are worse compared to experiment). The 6-31G SCF frequencies are in generally good agreement with the DZ SCF predictions, although the former method gives smaller frequencies for CCC bendings: 6.7% for butatriene and 8.3% for pentatetraene.

However, these two basis sets give vastly different results for butatriene when used with methods including electron correlation. Specifically, the 6-31G MP2 and 6-31G CISD methods produce frequencies consistently higher than the respective DZ MP2 and DZ CISD methods, except for the CCC bending frequencies (Tables 7 and 8). In fact, when electron correlation is incorporated through the MP2 method, the 6-31G MP2 predicted frequency for the (b_{2g}) CCC bending in C_4H_4 is imaginary (286i cm^{-1}), while the DZ MP2 value is real (517 cm^{-1}). When the CISD method is used, both the DZ and 6-31G basis sets predict real vibrational frequencies for the CCC bending in butatriene though they differ greatly in value (176 cm^{-1} by 6-31G and 552 cm^{-1} by DZ, Table IX). But for pentatetraene, the 6-31G CISD method predicts one imaginary e frequency (560i cm^{-1}), while all DZ CISD frequencies are real (Tables IX). These findings are very surprising since 6-31G and DZ are generally considered to be of comparable quality.

The electron correlation methods used here (MP2 and CISD) also predict significantly different vibrational frequencies for C_4H_4 and C_5H_4 (Tables VII and VIII), particularly for vibrations involving CCC bending. For instance, all of the DZ MP2 frequencies for C_4H_4 are lower than the DZ CISD ones (with an average difference of 4.2%, Table VII), and for the CCC bendings the differences amount to 4.9–14.1%. This difference is even larger when the 6-31G basis set is used. In this case, the b_{2g} CCC bending frequencies for C_4H_4 obtained from the MP2 (286i cm^{-1}) and CISD (176 cm-1) methods differ qualitatively. The 6-31G MP2 frequencies for C_5H_4 are also always lower than the corresponding 6-31G CISD values (Table VIII, average difference 6.7%).

Thus, two rather surprising discoveries were made concerning the theoretical vibrational frequencies for CCC bending in C_4H_4 and C_5H_4: (1) the DZ and 6-31G basis sets are vastly different in predicting these frequencies; (2) the MP2 and CISD methods are also significantly different in this respect. Since the CCC bending frequencies obtained from the 6-31G basis set are lower than those from the DZ basis set and the same frequencies from the MP2 method are lower than those from the CISD method, it is understandable that the 6-31G MP2 method employed by Liang and Allen[2] gave imaginary CCC bending frequencies in C_4H_4 and C_5H_4, while the DZ CISD method used here yields real frequencies. It should be noted that Pople's basis sets (6-31G, sometimes augmented by a set of polarization functions) and the perturbation methods (e.g. MP2) are used almost exclusively in other ab initio studies[2,21,22,24,25] of the bending of cumulated double bonds.

3.5. Results from a Triple-ζ Basis Set. Considering the unexpected large differences between the 6-31G and DZ basis sets, it was decided to adjudicate this dispute using the Huzinaga–Dunning triple-ζ basis set (TZ, 10s6p/5s3p on carbon and 4s/3s on hydrogen). A scale factor of 1.2 applied to the exponents of the hydrogen primitives),[34] which is more complete than either

Table IX. Experimental (Anharmonic) and Theoretical (Harmonic) Vibrational Frequencies (cm^{-1}) for the b_{1g} CH_2 Rocking, the b_2 CH_2 Wagging, CCC Bendings in C_4H_4, and CCC Bendings in C_5H_4

	SCF					CISD				MP2			
	DZ	DZ+d	DZP	6-31G	TZ	DZ	DZ+d	6-31G	TZ	6-31G	DZ	TZ	exp[a]
rock	1144	1106	1108	1162	1162	1066	1045	1095	1110	1072	1035	1090	663
wag	1075	1014	1009	1079	1082	913	894	965	946	916	844	886	544
						CCC Bendings in C_4H_4							
sym													
b_{1g}	426	371	371	439	447	333	295	302	331	216	286	263	234
b_{1u}	255	240	241	238	238	226	223	191	188	177	215	167	(?)
b_{2g}	646	603	603	603	642	552	539	176	451	286i	517	353	330
b_{2u}	248	238	238	250	247	221	217	219	218	207	210	205	215
						CCC Bendings in C_5H_4							
sym													
e	626	561	562	581	632	550	505	560i	382	754i	516	177i	
e	392	357	360	386	386	341	314	289	262	237	311	305	
e	169	159	160	155	155	156	150	134	124	121	149	127	

[a] From: Miller, F. A.; Matsubara, I. *Spectrochim. Acta* **1966**, *22*, 173. The b_{1u} (or b_{2u}) CCC bending was not observed (see text).

Table X. Theoretical and/or Experimental Harmonic Vibrational Frequencies (cm^{-1}) of C_2H_4, C_3H_4, C_4H_4 and C_5H_4 (Data in Parentheses Show the Symmetry)

	C_5H_4	C_4H_4		C_3H_4	C_2H_4	
vibration	DZ+d CI[a]	exp[b]	DZ+d CI[a]	exp[c]	exp[d]	DZP CI[e]
C–H str	3350 (e)	3080	3342 (b_{2u})	3214 (e)	3234	3349 (b_{2u})
		3059	3342 (b_{1g})		3232	3321 (b_{1g})
	3251 (a_1)	2995	3242 (a_g)	3141 (a_1)	3153	3252 (a_g)
	3250 (b_2)	2994	3242 (b_{3u})	3132 (b_2)	3147	3226 (b_{3u})
C_{sp}–C_{sp} str	2305 (b_2)	2079	2255 (a_g)			
	770 (a_1)					
C_{sp}–C_{sp^2} str	2011 (a_1)	1608	1733 (b_{3u})	1989 (b_2)		
	1365 (b_2)	878	919 (a_g)	1472 (a_1)	1655[f]	1737[f] (a_g)
twist	718 (b_1)	736	792 (a_u)	866 (b_1)	1044	1070 (a_u)
CH_2 scissor	1583 (b_2)	1430	1532 (a_g)	1424 (b_2)	1473	1518 (b_{3u})
	1507 (a_1)	1370	1461 (b_{3u})	1089 (a_1)	1370	1410 (a_g)
CH_2 rock	1048 (e)	1060	1076 (b_{2u})	1019 (e)	1245	1273 (b_{1g})
		663[g]	1045 (b_{1g})		843	842 (b_{2u})
CH_2 wag	886 (e)	854	896 (b_{1u})	858 (e)	969	983 (b_{1u})
		544[g]	894 (b_{2g})		959	885 (b_{2g})
CCC bend	505 (e)	330[g]	539 (b_{2g})	356 (e)		
	314 (e)	234[g]	295 (b_{1g})			
	150 (e)	NA	223 (b_{1u})			
		215	217 (b_{2u})			

[a] This work. [b] From: Miller, F. A.; Matsubara, I. *Spectrochim. Acta* **1966**, *22*, 173. [c] From: Hegelund, F.; Ducan, J. L.; McKean, D. C. *J. Mol. Spectrosc.* **1977**, *65*, 366. [d] From: Ducan, J. L.; McKean, D. C.; Mallinson, P. D. *J. Mol. Spectrosc.* **1973**, *45*, 221. [e] From: Lee, T. J.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 7062. [f] The C_{sp^2}–C_{sp^2} stretch. [g] Uncertain experimental assignments; see ref 5.

6-31G or DZ, was employed to study the geometry and vibrational spectra for butatriene and pentatetraene (Tables VI–VIII). The TZ MP2 frequencies were evaluated via finite differences of analytic gradients with GAUSSIAN 88.[39]

The TZ predicted geometries are very close to the corresponding ones obtained with the 6-31G basis set. But the TZ basis set gives considerably shorter bond lengths for these molecules than does the DZ basis set. For instance, the central C═C distance in C_4H_4 is 1.280 Å by the TZ MP2 method, a result that is close to the 6-31G MP2 value (1.287 Å) but is almost 0.02 Å shorter than the DZ MP2 value (Table VI).

Generally speaking, the TZ basis set does not strongly confirm either the DZ or the 6-31G basis set in predicting vibrational frequencies for C_4H_4 and C_5H_4. There is no simple trend about the SCF frequencies obtained from the 6-31G, DZ, and TZ basis sets. When the MP2 and CISD methods are used, most of the TZ predicted frequencies lie between those from the 6-31G and DZ basis sets, particularly for the CCC bending frequencies. However, the TZ basis does demonstrate that the 6-31G set is qualitatively wrong in its description of the CCC bending vibration of butatriene. Thus, for the b_{2g} CCC bending mode of butatriene, 6-31G MP2 gives an imaginary frequency (286i cm^{-1}), while TZ MP2 gives a real (353 cm^{-1}) albeit significantly lower frequency than the DZ MP2 method (517 cm^{-1}) (Table IX). Actually, the TZ basis predicted CCC bending frequencies for C_4H_4 are consistently lower than those by the DZ basis set when electron correlation is included (the differences are 2–32% for MP2 and 1–18% for CISD). This shows that the theoretical bending frequencies of cumulated C═C double bonds are extremely sensitive to basis sets.

As is the case for the 6-31G and DZ basis sets, the MP2 predicted vibrational frequencies are also consistently lower than those from the CISD method when the TZ basis set is used. The differences range from 1.0 to 21.7% with an average of 5.5% (for C_4H_4). Again, large differences are found in frequencies concerning CCC bending. Similar observations apply to C_5H_4 as well.

4. Discussion

As the last section shows, the vibrational frequencies for C_4H_4 and C_5H_4 obtained from different theoretical methods differ significantly and large discrepancies exist between theory and experiments. In the following, we shall discuss a few controversial

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[39] GAUSSIAN 88: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian, Inc.; Pittsburg PA.

problems in detail by, particularly, comparing the theoretical and/or experimental harmonic vibrational frequencies for the analogous compounds, C_2H_4, C_3H_4, C_4H_4, and C_5H_4 (Table X).

4.1. CH_2 Rocking and Wagging in C_4H_4. Table IX shows that all of the theoretical methods are fairly consistent in predicting the gerade (Raman active) CH_2 rocking and wagging frequencies in C_4H_4. The SCF values from different basis sets fall in the range of 1108–1162 cm^{-1} for CH_2 rocking and 1009–1082 cm^{-1} for CH_2 wagging. Different correlation methods also agree on these two frequencies (range 1035–1095 cm^{-1} for CH_2 rocking and 844–965 cm^{-1} for CH_2 wagging). However, the experimental assignments (633 and 544 cm^{-1} for CH_2 rocking and wagging, respectively) are much lower than these theoretical predictions. We believe that Miller and Matsubara's Raman assignments for these two vibrations may be too low (as they admitted) since (1) our DZ+d CISD predictions for the IR active CH_2 rocking and wagging frequencies in the same molecule are in good agreement with their IR spectrum analysis (within 5%) and (2) the corresponding experimental harmonic vibrational frequencies in allene[40] are 1019 (CH_2 rock) and 858 cm^{-1} (CH_2 wagging), which are only 2.5 and 4.0% lower than our DZ+d CISD values for butatriene (Table X). The CH_2 rocking and wagging frequencies (either IR or Raman active) in C_2H_2 are slightly lower than those in allene but are still significantly higher than Miller and Matsubara's assignments (Table X).

4.2. C=C Stretches in C_5H_4. The two highest C=C stretching frequencies of pentatetraene have been estimated empirically[41] to be 2100 (b_2) and 1600 (a_1) cm^{-1}. Ripoll[15,16] observed two bands at 2085 and 1660 cm^{-1} (along with four other bands) in the IR spectrum and he attributed these two frequencies to C=C stretchings. Our best theoretical method (DZ+d CISD) predicts two IR active bands for C=C stretches at 2305 and 1365 cm^{-1}. Thus, the empirical estimate, Ripoll's experimental observation, and our theoretical prediction agree on the IR active C=C stretch with higher frequency (at about 2100 cm^{-1}, if the theoretical value is scaled down by about 8%). However, there are serious problems with the other frequency. First, one should note that the empirically estimated 1600-cm^{-1} band, with a_1 symmetry, should be IR inactive if C_5H_4 is linear! Therefore, the fact that there is an IR absorption at 1660 cm^{-1} should not be taken as supporting evidence for the observation of linear pentatetraene as Ripoll thought.[15,16] Second, as pointed out above, the observed frequency at 1660 is too high for the other IR active C=C stretch when compared to the DZ+d CISD prediction (1365 cm^{-1}). Third, the empirically estimated (a_1) C=C stretch frequency of 1600 cm^{-1} is too low compared to the corresponding DZ+d CISD value (2011 cm^{-1}).

Concerning the controversy about the 1660-cm^{-1} band, two observations are worth mentioning: (1) No band has been reported in the 1600-cm^{-1} region for all substituted pentatetraenes synthesized so far.[17–19] (2) This band falls in the range for a typical C=C stretch in alkenes[42] (1640–1680 cm^{-1}) and therefore it would show up *if* C_5H_4 is bent rather than linear.

As for the empirical estimate, it is unfortunate that the specific method used in the estimation was not reported, though it is most likely a force field calculation. In this connection, we note that the DZ+d CISD evaluated force constants for the C_1–C_2 (i.e., C_{sp}–C_{sp}) and C_2–C_4 (C_{sp}–C_{sp^2}) stretches are *not* equal and they are 12.12 and 10.67 mdyn/Å (not symmetrized[42]), respectively. These values are very close to those for corresponding C–C stretches in butatriene with the same method (12.38 and 10.48 mdyn/Å).[43] The above (harmonic) C_{sp}–C_{sp^2} stretch force constants for butatriene and pentatetraene are just slightly higher than the experimental harmonic C_{sp}–C_{sp^2} stretch force constants for allene[40] (10.34 mdyn/Å for the a_1 symmetry mode and 9.24 mdyn/Å for the b_2 symmetry mode).

On the other hand, the theoretical C_{sp}–C_{sp^2} stretching frequencies in C_5H_4 (2011 and 1365 cm^{-1}) are reasonably close to the experimental harmonic C_{sp}–C_{sp^2} stretching frequencies[40] in C_3H_4 (1989 and 1472 cm^{-1}, Table X). Moreover, the DZ+d CISD method proved to be successful in predicting the C=C stretching frequencies in C_2H_4 and C_4H_4 (Table X). Thus, the DZ+d CISD predicted C=C stretching frequencies for C_5H_4 should be reasonably reliable.

4.3. CCC Bending in C_4H_4 and C_5H_4. Table IX shows that the experimental and theoretical frequencies for b_{2g} CCC bending in C_4H_4 differ greatly, while theory and experiment[5] agree on the other CCC bending frequencies. Different theoretical methods also disagree dramatically on this vibration. Especially, the 6-31G basis set in conjunction with the MP2 method predicts an imaginary frequency for the b_{2g} CCC bending mode of butatriene. When used with the CISD method, this basis set also gives a frequency that is too low, though real, for this motion. However, all of the Huzinaga–Dunning basis sets predict the b_{2g} CCC bending to possess the highest CCC bending frequency (Table IX). A qualitative theoretical analysis[2] suggests that the b_{1u} CCC bending should have the lowest CCC bending frequency. This agrees with results obtained from the Huzinaga–Dunning basis sets but not with those from the 6-31G basis set.

It should be noted that all theoretical methods predict two IR active bands (corresponding to b_{1u} and b_{2u} CCC bendings) in the 200-cm^{-1} vicinity with medium to strong intensities; but only one peak (experimentally assigned to b_{2u} arbitrarily[5]) was present in the gas-phase IR spectrum reported.

All of the theoretical methods show that the lowest frequency normal mode for C_5H_4 involves CCC bending at the central carbon, as is expected.[2] However, the 6-31G MP2, TZ MP2, and 6-31G CISD methods predict an imaginary frequency for this vibration, while all other theoretical bending frequencies are real. Considering the small magnitude of the CCC bending frequencies obtained with the TZ basis set with the MP2 or CISD method, one should not draw definitive conclusions regarding the linearity of the carbon chain in C_5H_4, since adding polarization functions will certainly reduce these frequencies (as discussed above). Thus, at least TZP or TZ2P basis sets must be used in conjunction with methods including electron correlation to solve this problem theoretically. Unfortunately, this is a formidable task at the present time.

4.4. Possible Vibrational Reassignments. At the suggestion of Professor F. A. Miller, alternative assignments of the observed Raman bands at 663 and 554 cm^{-1} were considered. Clearly the observed feature at 544 cm^{-1} is a better fit to the theoretical CCC bending harmonic frequency predicted at 539 cm^{-1} (DZ+d CI). Although we would have guessed an experimental fundamental $\nu = 490$ cm^{-1} (corresponding to the theoretical harmonic frequency $\omega = 539$ cm^{-1}), this assignment to b_{2g} symmetry fits the fact that the 544-cm^{-1} Raman feature is not observed in the IR spectrum (b_{2g} fundamentals are forbidden in the IR spectrum).

Assignment of the Raman feature at 663 cm^{-1} becomes even more speculative. One conceivable option is that the experimental 663-cm^{-1} band is the a_u fundamental (DZ+d CI prediction 792 cm^{-1}). However, this forces the laboratory feature at 736 cm^{-1} to be assigned to the higher b_{2g} fundamental (DZ+d CISD prediction 894 cm^{-1}). Clearly these reassignments are treacherous. Vibrational frequency predictions at higher levels of theory would be helpful, as would be theoretical Raman intensities.

5. Conclusions

A few very important conclusions may be drawn from the present ab initio study.

(1) Although the theoretical predictions obtained from the DZ+d CISD method agree with Miller and Matsubara's assignment[5] for most of the vibrations of butatriene, their tentative assignments for three of the Raman bands seem to be questionable. Specifically, their assigned (Raman) frequencies for CH_2 rocking

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(43) The force constants in totally symmetrized internal coordinates are the following. Butatriene: 12.38 (a_g, C_{sp}–C_{sp}), 10.31 (a_g, C_{sp}–C_{sp^2}), and 10.64 (b_{3u}, C_{sp}–C_{sp^2}) Pentatetraene: 12.93 (a_1, C_{sp}–C_{sp}), 11.31 (b_2, C_{sp}–C_{sp}), 10.76 (a_1, C_{sp}–C_{sp^2}), and 10.58 (b_2, C_{sp}–C_{sp^2}) mdyn/Å.

and wagging, and b_{2g} CCC bending differ from our DZ+d CISD predictions, by more than 60% in some cases.

(2) For pentatetraene, there are significant discrepancies between the present study and existing experiments.[15,16] In particular, the observed 1660-cm^{-1} band appears to be misassigned since it is too high for the b_2 C=C stretching according to the DZ+d CISD results. In fact, this observed band, as well as two other observed bands at 1140 and 910 cm^{-1}, does not seem to fit any normal mode when compared with the DZ+d CISD harmonic vibrational frequencies of the *linear* structure.

(3) It is found that the theoretical vibrational frequencies for C_4H_4 and C_5H_4 are extremely sensitive to the basis set and the correlation method. Thus, the frequencies for the CCC bending in C_4H_4 and C_5H_4 obtained with the DZ and 6-31G basis sets are vastly different, particularly when electron correlation is explicitly included. It is also shown that the MP2 and CISD methods give significantly different frequencies for the same vibration. Specifically, the CCC bending frequencies obtained from the 6-31G basis set and from the MP2 method are significantly lower than those obtained from the DZ basis set and from the CISD method, respectively. Thus, when the 6-31G basis set is used with the MP2 method, the predicted vibrational frequencies for the bending of cumulated double bonds are much lower than those from the DZ basis set and the CISD method. Sometimes the corresponding diagonal force constants differ even in sign. The TZ basis set predicts vibrational bending frequencies for C_4H_4 and C_5H_4 in qualitative agreement with neither the 6-31G nor the DZ basis. But it gives significantly lower CCC bending frequencies than does the DZ basis sets. Therefore, extreme caution must be exercised in theoretical studies of bending of cumulated double bonds.

In conclusion, it seems that the structure of butatriene (C_4H_4) is linear, since the DZ+d CISD predicted frequencies for the linear structure are in good agreement with the IR and Raman spectra (except for a few uncertain Raman assignments) and it is only the 6-31G MP2 method which predicts an imaginary frequency for the bending of the linear structure. However, it is not clear whether the linear structure of pentatetraene (C_5H_4) is an energy minimum since serious discrepancies remain to be solved. (1) Most of the observed IR bands for C_5H_4 do not seem to agree with any DZ+d CISD predicted frequencies for the linear structure. (2) Theoretical predictions vary significantly. Specifically, the 6-31G CISD (as well as the 6-31G MP2 and TZ MP2 methods) gives an imaginary frequency for the bending of the linear structure. Other more reliable methods predict real frequencies for this structure; but the small magnitude of the TZ predicted CCC bending frequencies calls for more theoretical studies with better basis sets. At the highest level of theory considered here (DZ+d CISD), the predicted e symmetry CCC bending frequency is only 150 cm^{-1}. Since the present work has almost reached the limit of the current technology in quantum chemistry, experimental work on this molecule may be more effective in determining the ground-state structure of pentatetraene.

As for the question whether long cumulenes are more apt to bend, the answer is certainly positive from the present study and thus agrees with Liang and Allen's analysis[2] but not with that of Trinquier and Malrieu.[1]

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Applications and Evaluations of IGLO Chemical Shift Calculations for Organolithium Compounds

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Abstract: The individual gauge for localized orbitals (IGLO) method has been applied to calculate the ^{13}C NMR shifts of numerous organolithium compounds. For the compounds existing as monomers in solution, the accord with experiment is satisfactory. The dependence of the calculated chemical shifts on aggregation and solvation was studied systematically for methyl-, vinyl-, and propynyllithium: these effects are shown to be most important for the unsaturated compounds but tend to cancel. For the aliphatic compounds, the effect of solvation and aggregation on δ ^{13}C is smaller. Hence, even IGLO chemical shifts calculated for isolated saturated monomers give acceptable agreement with the experimental values for aggregated species. Calculated ^{13}C chemical shifts for unsaturated organolithium compounds can be related to the π-electron density analogous to the Spiesecke–Schneider relationship. In some cases, IGLO calculations may be used to distinguish between structural possibilities; e.g., in benzyllithium the lithium cation is attached mainly to the benzylic and ipso carbons.

Introduction

Although organolithium compounds are important synthetic reactants,[1] their detailed characterization has been difficult. Because of the high degree of ionic character, these polar molecules often are considered to be equivalents to "carbanions". However, very few organolithium compounds exist as separated ions or as ion pairs; most exhibit various degrees of aggregation and solvation in the solid state and in solution.[2] The degree of aggregation can

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