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Articles

Molecular Structure of 3,3-Diethylpentane (Tetraethylmethane) in the Gas Phase As Determined by Electron Diffraction and ab Initio Calculations

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The molecular structure of 3,3-diethylpentane (tetraethylmethane) in the gas phase has been determined by electron diffraction and ab initio calculations at the MP2/6-31G* level. Five local minima on the potential energy surface were located, but only two have significant populations at room temperature. The experimental distribution of conformers was found to be 66(2)% with D_{2d} symmetry and 34(2)% with S_4 symmetry, corresponding to an energy difference $\Delta H°$ in favor of the D_{2d} form of 3.3(2) kJ mol^{-1}. The molecule shows significant distortion from regular tetrahedral coordination at the central carbon atom, with two CCC angles in the D_{2d} form reduced to 106.7(8)° and two angles in the S_4 form increased to 110.9(4)°. These distortions are attributed to asymmetry of the electron density distribution around the CH_2 groups.

Introduction

Many important properties are crucially dependent on molecular shape, so methods for controlling conformations about C−C bonds therefore have wide significance. The conformational control of a structure by the incorporation of rings is well-known, but methods for the control of conformation in acyclic molecules are less thoroughly developed. Simple acyclic molecules can be surprisingly complex conformationally. Thus, *n*-hexane has 12 distinct conformations, of which six are populated to the extent of 4% or more at 298 K, according to ab initio MP4SDQ/6-31G*//MP2/6-31G* calculations.[1] The complexity of this case is in striking contrast to that of cyclohexane, for which only two conformations (chair and boat) are possible.

In general, the conformations of acyclic molecules can only be controlled by using nonbonding interactions, and a number of examples of this control have appeared in recent years,[2] especially in the elegant work of Still[3] and Hoffmann. Hoffmann has discussed the use of conformational control elements in several interesting papers.[4−7] He has pointed out that the most effective control often amounts to the creative use of g^+g^- or *syn*-pentane[8] interactions, which produce a destabilization of between 6 and 13 kJ mol^{-1}.

In 1990, Alder, Maunder, and Orpen reported that quaternary atoms provided substantial conformational control over the adjacent bonds.[9] Simple conformational analysis predicts that 3,3-diethylpentane (CEt_4) will have only two low-energy conformations, with D_{2d} and S_4 symmetry.[10] All other conformations suffer from g^+g^- interactions and are predicted by molecular mechanics calculations to be barely populated at room temperature.

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Table 1. Experimental Data

camera distance/mm	weighting function/nm^{-1}					correlation parameter	scale factor k[a]	electron wavelength/pm[b]
	Δs	s_{min}	sw_1	sw_2	s_{max}			
285.90	2	30	50	118	140	−0.055	0.750(6)	5.673
128.24	4	100	120	292	344	0.362	0.648(8)	5.674

[a] Figures in parentheses are estimated standard deviations of the least significant digits. [b] Determined by reference to the scattering pattern of benzene vapor.

In 4,4-diisopropylheptane (CPr^i_4) there are also only D_{2d} and S_4 low-energy conformations, showing that the conformational control extends to next-to-adjacent bonds, and evidence for this was provided by examination of the many structures of NEt_4^+ and $NPr^i_4{}^+$ ions reported in the Cambridge Crystallographic Database. Calculations further suggest that there will be substantial barriers to the interconversion of the D_{2d} and S_4 conformers, with several possible pathways, and a study of the solid-state ^{13}C NMR of CEt_4 supports this.[11] The extensive conformational control provided by quaternary centers should be useful in designing novel polymers, and Alder et al.[12] reported the preparation of $(Pr^i_2CCH_2CH_2CH_2)_n$ via regiospecific ring-opening polymerization of 3,3-diisopropylcyclobutene and provided evidence that this polymer has unusual properties. A full discussion of the conformational effects of quaternary centers, including the mechanisms for interconversion of the D_{2d} and S_4 conformers, has recently appeared.[13]

The simplest molecule to which these conformational considerations apply is 3,3-diethylpentane. In this paper we describe its molecular structure in the gas phase, as determined by electron diffraction and by ab initio calculations.

Experimental Section

Synthesis. NMR spectra were obtained on a JEOL JNM-GX270 spectrometer in $CDCl_3$ solvent. Chemical shifts are reported in ppm relative to an internal tetramethylsilane reference for ^1H and ^{13}C spectra.

Preparation of 3,3-Diethylpentane.[14,15] Diethylzinc (1.0 M soln. in hexane, 92.5 mL, 92.5 mmol) was added dropwise to a solution of 3-chloro-3-ethylpentane (24.9 g, 0.185 mol) in pentane (30 mL) under an atmosphere of dry nitrogen. This was refluxed for 1 h and then hydrolyzed with dilute HCl. The organic layer washed twice with concentrated H_2SO_4, neutralized ($NaHCO_3$), dried ($MgSO_4$), and then filtered through activated silica. The product was collected by distillation (bp 130−140 °C) to give 10 g (40%) of 3,3-diethylpentane: δ_H (270 MHz, $CDCl_3$) 1.16 (q, 8H, $J = 7.5$ Hz), 0.72 (t, 12H, $J = 7.5$ Hz); δ_C (68 MHz, $CDCl_3$) 37.02, 26.09, 7.42.

Theoretical Methods. A graded series of ab initio molecular orbital calculations was undertaken to predict geometric parameters for 3,3-diethylpentane and to obtain theoretical harmonic force fields, from which estimates of vibrational amplitudes could be obtained using the ASYM40 program.[16] All calculations were carried out on a DEC Alpha APX 1000 workstation using the Gaussian suite of programs.[17] Geometry optimizations were performed using standard gradient techniques at the SCF level of theory using 3-21G*[18−20] and 6-31G*[21−23] basis sets. The larger basis set was subsequently adopted for calculations at the MP2(FC) level of theory.

Vibrational frequency calculations were performed on all located stationary points at the HF/3-21G* and HF/6-31G* levels to verify structures as local minima on the potential energy surface. The force fields used in GED refinements were constructed using the results of HF/6-31G* calculations. Force constants were scaled by factors of 0.90, 0.85, and 0.80 for bond stretches, angle bends, and torsions, respectively.

Electron Diffraction Measurements. Electron diffraction scattering patterns were recorded using the Edinburgh gas diffraction apparatus[24] on Kodak Electron Image plates with the nozzle tip and the sample both at a temperature of 293 K. The accelerating voltage of the electron beam was about 44.5 kV. Three plates from the long (286 mm) and three from the short (128 mm) camera distance were selected for the analysis. Scattering patterns for benzene were also recorded, so that calibration of the electron voltage and nozzle-to-plate distances could be performed. Data were obtained in digital form using the automatic Joyce-Loebl MDM6 microdensitometer at the EPSRC Laboratory, Daresbury, U.K.[25] The programs used for the data reduction[25] and least-squares refinements,[26] applied to molecular intensities modified by s^4, have been described previously. Published complex scattering factors[27] were employed. The weighting points used in setting up the off-diagonal weight matrix, s ranges, scale factors, correlation parameters, and electron wavelengths are all presented in Table 1.

Results

Theoretical Calculations. Considering only *anti* (A) and *gauche* (G) conformations, there are 81 possible combinations of dihedral angles for the four ethyl groups

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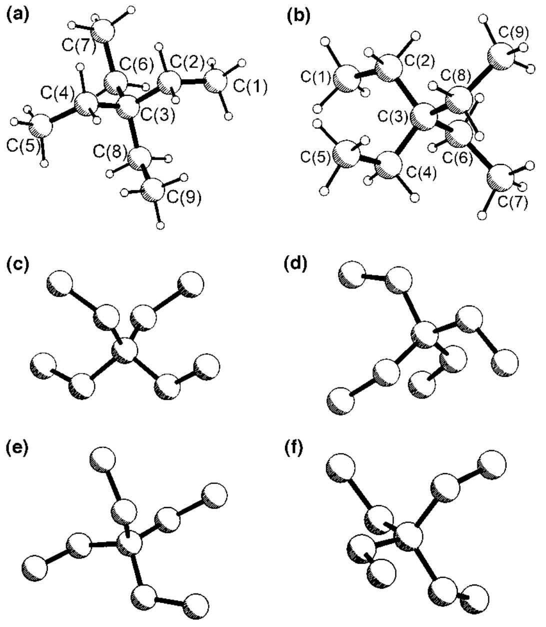

Figure 1. Views of six possible conformers of 3,3-diethylpentane, showing the atom numbering scheme: (a) D_{2d} symmetry; (b) S_4; (c) C_2; (d) C_s (transition state); (e) C_1; (f) C_1.

attached to the central carbon atom of 3,3-diethylpentane. However, many of these are equivalent, and there are just six nonequivalent structures, two of which have overall C_1 symmetry (each with multiplicity 24) and one with each of C_s, C_2, S_4, and D_{2d} symmetries (Figure 1), with multiplicities of 12, 12, 6, and 3, respectively.

Vibrational frequency calculations performed at the HF/3-21G* and HF/6-31G* levels showed that five of the six conformers represent local minima on the potential energy surface, the exception being **4** (C_s symmetry), which is predicted to be a transition state. Only two of the five local minima were found to have significant gas-phase populations at room temperature, and so selected geometric parameters are reported only for conformers **1** (D_{2d} symmetry) and **2** (S_4 symmetry), at the three levels of calculation employed (Table 2). The predicted molecular geometries are notable for their insensitivity to the theoretical treatment adopted, with improvements beyond preliminary calculations undertaken at the HF/3-21G* level leading to changes in bond lengths and bond angles which never exceed about 1 pm or 1° in either structure.

As might be expected, bonds to the central carbon in both structures are predicted to be longer than other C−C bonds by around 1.5 pm, and the degree of distortion from regular tetrahedral geometry at C(3) is small. Structural differences between conformers **1** and **2** are also small; for example, the bond lengths to the central carbon atom in the two structures are indistinguishable at the MP2/6-31G* level and the outer [C(1)−C(2)] bonds differ in length by only a few tenths of a picometer. Bond angles about the central carbon exhibit slightly larger differences; C(2)−C(3)−C(4) and C(2)−C(3)−C(5) are predicted to be 106.6 and 111.0° for **1** compared to 110.8 and 108.8° for **2** (MP2/6-31G*). The remaining skeletal angle, C(1)−C(2)−C(3), was predicted to be 116.6 and 116.4° (MP2/6-31G*) for structures **1** and **2**, respectively, and the S_4 structure **2** is predicted to have the ethyl groups twisted by about 126° away from the positions in the D_{2d} structure.

The relative energies (with and without corrections for zero-point energy) of the five local minima are presented in Table 3. Structure **1** was always found to have the lowest energy by more than 3 kJ mol^{-1}. The energies of all other structures relative to **1** proved to be fairly insensitive to the adopted theoretical method; values of relative energies always fell within a range of less than 2 kJ mol^{-1}. The energy ordering of the isomers did not alter with improvements in the theoretical treatment. At the highest level of theory [MP2/6-31G* + ZPE(HF/6-31G*)], the energy ordering of isomers is predicted to be **1** < **2** < **6** < **5** < **3** corresponding to a predicted gas-phase conformational mixture comprising 63.6% **1**, 32.8% **2**, 2.4% **6**, 1.1% **5**, and <0.1% **3** at 293 K.

Molecular Model. In the six possible conformers there are only four groups of different C(CC)C distances. These are ca. 250, 360, 440, and 500 pm, corresponding to g^+g^-, g^+g^+, *ag*, and *aa* interactions. There are three of the unfavorable short 1,3 interactions (g^+g^-) in conformer **6**, two in conformer **5**, and one in each of conformers **3** and **4**, and the MP2/6-31G* calculations predict that these give these conformers sufficiently high energies that only the D_{2d} and S_4 forms need to be considered in the molecular model, despite the lower multiplicities of these last two forms. Moreover, the C_s form turned out to be a saddle point of the first order on its potential hypersurface.

In light of these results, an electron diffraction model taking just two conformers into account was constructed. With the exception of the CCC angles at the central carbon atom, the computed values of the geometrical parameters for the two forms differed only negligibly. Small differences between HCH and CCH angles in the two conformers were fixed as calculated, but otherwise identical sets of eight of the nine independent geometrical parameters were used for generating the D_{2d} and S_4 geometries.

Five parameters were needed to model the CC_4 cores. These are the mean length of the two types of C−C bonds, *r*[C(2)−C(3)] and *r*[C(1)−C(2)], the difference between these two distances (p_1, p_2), and three angles defining CCC angles. Taking the S_4 axis to bisect the angles

Table 2. Selected Geometric Parameters (*r* in pm, Angles in deg) for 1 and 2

	1, D_{2d} symmetry			**2**, S_4 symmetry		
parameter	HF/3-21G*	HF/6-31G*	MP2/6-31G*	HF/3-21G*	HF/6-31G*	MP2/6-31G*
C(2)−C(3)	155.3	155.0	154.2	155.3	155.1	154.3
C(1)−C(2)	154.3	153.1	152.8	154.4	153.3	153.0
C−H (mean)	108.4	108.5	109.5	108.4	108.5	109.5
C(2)−C(3)−C(4)	106.5	106.2	106.6	111.1	111.2	110.8
C(2)−C(3)−C(5)	111.0	111.1	111.0	108.7	108.6	108.8
C(1)−C(2)−C(3)	116.3	117.4	116.6	116.1	117.4	116.5
C−C−H (mean)	110.2	110.3	110.2	110.2	110.3	110.2
C(1)−C(2)−C(3)−C(4)	180.0	180.0	180.0	54.7	54.7	54.3

Table 3. Predicted Relative Energies ($\Delta H°$ in kJ mol^{-1}) and Gas-Phase Composition of the Conformers of 3,3-Diethylpentane[a]

	relative energy			
conformer	HF/3-21G*	HF/6-31G*	MP2/6-31G*	wt %
1 (D_{2d})	0 (0)	0 (0)	0 (0)	63.6
2 (S_4)	2.5 (2.8)	3.2 (3.5)	3.1 (3.3)	32.8
3 (C_2)	27.8 (28.6)	24.2 (25.2)	24.0 (25.0)	0.0
4 (C_s)	50.1 (49.6)	46.9 (46.0)	47.3 (46.4)	0.0
5 (C_1)	15.5 (15.7)	14.3 (14.7)	14.6 (14.9)	1.1
6 (C_1)	14.3 (14.9)	13.0 (13.7)	12.4 (13.0)	2.4

[a] Numbers in parentheses are corrected for zero-point energy. MP2/6-31G* energies are corrected for zero-point energy using HF/6-31G* frequencies.

C(2)C(3)C(4) and C(6)C(3)C(8), these two angles at the central carbon atom are different from the other four and are different in the two conformers, whereas the C(1)C(2)C(3) angle was the same for both conformers. The three parameters, p_3, p_4, and p_5, were therefore chosen to be the weighted mean of C(1)C(2)C(3), C(2)C(3)C(4) (D_{2d}), and C(2)C(3)C(4) (S_4) and the differences between this mean and the angles C(2)C(3)C(4) for the two separate conformers. All the individual CCC angles were then dependent parameters. A simplified model, in which the central angles C(2)C(3)C(4) in the two conformers were assumed to be equal, yielded parameters which were all well within 1 esd of those obtained for the D_{2d} conformer in the more sophisticated analysis.

Since the computed C−H bond lengths differed by less than 0.5 pm (in both forms, MP2/6-31G* level), only a single distance was used (p_6). The other hydrogen-defining parameters consisted of the HC(2)H bond angle, p_7, and the mean CCH bond angle, i.e., [2 × C(3)C(4)H + 3 × C(4)C(5)H]/5, p_8, and the associated difference, [C(2)C(1)H − C(3)C(2)H], p_9. (The differences between p_7 and p_9 for the two conformers were fixed at calculated values.) Local C_{2v} and C_{3v} symmetries were assumed for the $-CH_2-$ and CCH_3 groups, as only marginal deviations from these idealized symmetries were indicated by the ab initio calculations.

The final independent parameter was the percentage of the S_4 form, p_{10}. The whole set of the 10 independent parameters is presented in Table 4.

Refinement of the Structure. Refinement of the geometrical parameters commenced with the values calculated at the MP2/6-31G* level. Of the four difference parameters, only that between the outer CCC bond angle and the central CCC angle for the D_{2d} form (p_4) could refine freely; flexible restraints were applied to the other three and also to the angle HC(2)H.

Calculated vibrational amplitudes based on force fields constructed ab initio for both the D_{2d} and the S_4 forms served as the initial values for the refinements. The vibrational parameters associated with closely spaced distances were grouped in blocks, and where the computed amplitudes were very similar to one another they were assumed to be equal during the refinements. Where there were larger differences between the u values, they were constrained to maintain the calculated ratios. In addition, some amplitudes and groups of amplitudes were subject to flexible restraints (Table 5). In particular, almost all the amplitudes of the vibrations of the nonbonded C···C pairs of the less abundant S_4 form were refined under such conditions. Two amplitudes, u_{19} and u_{21}, refined to values significantly smaller than those calculated, but if they were fixed at or restrained to the higher values, u_{14} became unreasonably large. The final values are consistent with those for comparable atom pairs in related molecules.

Table 4. Experimental Geometrical Parameters (r_a) for a Mixture of the D_{2d} and S_4 Forms of $C(C_2H_5)_4$ (Distances in pm, Angles in deg)[a]

no.	parameter	value
p_1	{r[C(1)−C(2)] + r[C(2)−C(3)]}/2	154.28(5)
p_2	r[C(2)−C(3)] − r[C(1)−C(2)]	2.2(4)[b]
p_3	{[C(2)C(3)C(4), D_{2d}] + [C(2)C(3)C(4), S_4] +4 × [C(3)C(2)C(1), D_{2d} + S_4]}/6	112.9(4)
p_4	[C(3)C(2)C(1), D_{2d} + S_4] − [C(2)C(3)C(4), D_{2d}]	8.8(5)
p_5	[C(3)C(2)C(1), D_{2d} + S_4] − [C(2)C(3)C(4), S_4]	7.0(13)[b]
p_6	r(C−H)	112.4(1)
p_7	HC(2)H[c]	107.2(16)[b]
p_8	[2 × C(3)C(2)H[c] +3 × C(2)C(1)H]/5	108.3(3)[b]
p_9	C(2)C(1)H − C(3)C(2)H	2.1(8)[b]
p_{10}	% S_4	34.0
p_{11}	[C(3)C(2)C(1), D_{2d} + S_4]	115.5(5)
p_{12}	[C(2)C(3)C(4), D_{2d}]	106.7(8)[d]
p_{13}	[C(2)C(3)C(6), D_{2d}]	110.9(4)[d]
p_{14}	[C(2)C(3)C(4), S_4]	108.6(18)[d]
p_{15}	[C(2)C(3)C(6), S_4]	109.9(9)[d]
p_{16}	[C(2)C(1)H, D_{2d} + S_4]	109.1(5)[d]
p_{17}	[C(3)C(2)H, D_{2d}]	106.9(5)[d]
p_{18}	[C(3)C(2)H, S_4]	107.4(5)[d]

[a] Figures in parentheses are the estimated standard deviations. [b] Flexibly restrained (see Table 5). [c] The calculated difference of 0.5° between values of this angle in S_4 and D_{2d} conformers was assumed in the model. The value given here is for the D_{2d} form. [d] Dependent parameter.

Table 5. Flexible Restraints for $C(C_2H_5)_4$

restrained parameter	value (pm or deg)	uncertainty (pm or deg)
p_2	1.5	1.0
p_5	5.7	2.0
p_7	108.5	2.0
p_9	2.9	1.0
u_{12}	12.3	1.2
u_{20}	34.9	3.5
u_{21}	22.0	2.2
u_{22}	25.0	2.5
u_{23}	11.2	1.1
u_{24}	12.9	1.3
u_{26}	13.1	1.3
u_{28}	7.3	0.7

The relative abundances of the two conformers were determined by varying the proportions and recording the R factors. The lowest values ($R_G = 0.022$, $R_D = 0.025$) were found with 34% of the S_4 form, and Hamilton's R-factor test[28] gave a 95% confidence limit of ±4%, corresponding to an estimated standard deviation of 2%. This yields an energy difference ($\Delta H°$) of 3.3(2) kJ mol^{-1}.

Final refined parameters are given in Table 4 and interatomic distances and amplitudes of vibration in Table 6. Errors quoted in parentheses are estimated standard deviations obtained in the least-squares analyses. Our methods of analysis are designed to reduce systematic errors in electron wavelengths, camera distances, etc. to negligible levels and takes account of correlation between adjacent intensity data points. The SARACEN method removes the effects of correlation with parameters which otherwise would not be included in the refinement, and so we believe that these quoted errors are realistic esd's, with the normal statistical meaning. The most significant elements of the least-squares cor-

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Table 6. Final Interatomic Distances (r_a in pm)[a] and Root Mean Square Amplitudes of Vibration (u in pm) for the D_{2d} and S_4 Forms of $C(C_2H_5)_4$

			u[b]		
				force field	
	atom pair	r_a[b]	GED	D_{2d}	S_4
		(a) D_{2d} and S_4 Forms			
d_1	C(1)−C(2)	153.2(2)	5.1(1)	5.1	5.1
d_2	C(2)−C(3)	155.4(2)	5.1 (tied to u_1)	5.2	5.2
d_3	C(1)−H(11)	112.4(1)	7.2(1)	7.7	7.7
d_4	C(2)−H(21)	112.4(1)	7.2 (tied to u_3)	7.7	7.7
d_5	C(1)···C(3)	261.0(7)	8.0(2)	7.0	7.0
d_6	C(2)···C(4)	249.4(14)	8.0 (tied to u_5)	6.9	7.0
d_7	C(2)···C(6)	255.9(6)	8.0 (tied to u_5)	7.0	7.0
d_8	C(2)···H(11)	217.6(6)	11.1(2)	10.7	10.7
d_9	C(1)···H(21)	218.7(8)	11.1 (tied to u_8)	10.6	10.6
d_{10}	C(3)···H(21)	216.6(6)	11.1 (tied to u_8)	10.3	10.3
d_{11}	C(3)···H(11)	286.5(7)	20.2(11)	16.7	16.9
d_{12}	H(11)···H(12)	183.9(6)	13.0(11)[c]	12.3	12.3
d_{13}	H(21)···H(22)	180.9(19)	13.0 (tied to u_{12})	12.3	12.3
		(b) D_{2d} Form			
d_{14}	C(1)···C(7)	370.4(10)	26.7(26)	27.0	
d_{15}	C(1)···C(5)	520.3(15)	11.6(10)	8.1	
d_{16}	C(1)···C(6)	310.2(6)	12.7(8)	13.3	
d_{17}	C(1)···C(4)	391.4(13)	8.3(6)	7.3	
d_{18}	C(6)···H(11)	411.2(4)	19.6(14)	14.4	
d_{19}	C(6)···H(12)	348.1(7)	15.0(24)	30.0	
d_{20}	C(7)···H(11)	446.1(6)	38.6(32)[c]	34.9	
d_{21}	C(7)···H(12)	317.1(10)	21.8(23)[c]	38.7	
d_{22}	C(5)···H(12)	539.8(13)	20.2(17)[c]	17.5	
d_{23}	C(6)···H(22)	350.8(6)	10.3(10)[c]	11.2	
		(c) S_4 Form			
d_{24}	C(1)···C(7)	452.8(28)	14.2(11)[c]		12.9
d_{25}	C(1)···C(5)	367.6(38)	20.8 (tied to u_{14})		21.0
d_{26}	C(1)···C(6)	309.4(31)	11.8(12)[c]		13.1
d_{27}	C(1)···C(4)	306.4(31)	11.8 (tied to u_{26})		13.0
d_{28}	C(1)···C(8)	395.1(14)	7.9(7)[c]		7.3

[a] Other nonbonded C···H and H···H distances were included in the refinement, but they are not listed here. Their vibrational amplitudes were constrained to refining amplitudes above or were fixed at calculated values. [b] Least-squares standard deviations in the last digit are given in parentheses. [c] Flexibly restrained.

Table 7. Portion of the Least-Squares Correlation Matrix for the D_{2d} + S_4 Mixture of $C(C_2H_5)_4$ Showing All Elements ≥ 50%

	p_4	p_5	p_6	p_7	u_3	u_5	u_{11}	u_{14}	u_{23}	u_{24}	u_{26}	k_1	k_2
p_1			−53		54								
p_2	−53					68	69						
p_3		−81						−52					
p_4		59				−73	−58						
p_8				53									
p_9						50							
u_1					51							62	
u_3												62	68
u_5							63						
u_8							57						
u_{11}													56
u_{12}													−52
u_{16}											86		
u_{18}								68		58			
u_{19}									−60				
k_1													65

relation matrix are listed in Table 7. The excellent fit between the calculated and experimental molecular intensities is also shown by the difference molecular scattering (Figure 2) and radial distribution (Figure 3) curves. The experimental molecular geometries of the D_{2d} and S_4 forms agree extremely well with the theoretical results. The experimental data are also consistent with the calculated distribution of conformers, determined to be D_{2d}:S_4 = 66:34 at the MP2/6-31G* + ZPE (HF/6-31G*) level, ignoring small amounts of higher energy forms.

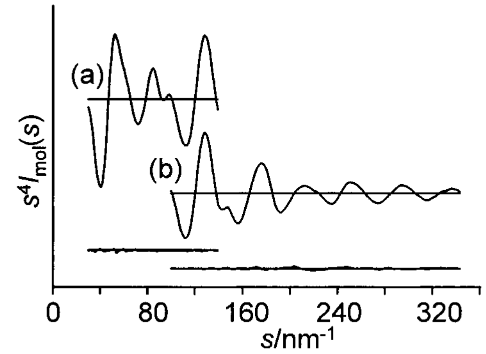

Figure 2. Observed and final weighted difference molecular-scattering intensity curves for 3,3-diethylpentane. Nozzle-to-plate distances were (a) 286 mm and (b) 128 mm.

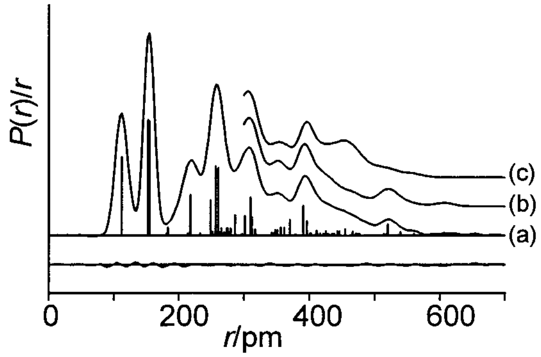

Figure 3. Observed and final weighted difference radial-distribution curves for 3,3-diethylpentane: curve a shows the experimental data, curve b the theoretical data for the D_{2d} conformer only, and curve c the theoretical data for the S_4 conformer only. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.00002s^2)/(Z_C - f_C)(Z_C - f_C)$.

Discussion

The structure of tetraethylmethane raises two important issues: the distribution of conformers and the deviations from regular tetrahedral angles at the central carbon atom. In general, tetrahedral molecules and ions of the type $M(CH_2X)_4$ adopt conformations with D_{2d} and S_4 symmetry, as other conformers are destabilized by g^+g^- interactions. In the present case the D_{2d} form is preferred, accounting for twice as many molecules as the S_4 form, even though its multiplicity is just 3, instead of 6. In $C(CH_2Cl)_4$ at 378 K the proportion of the D_{2d} conformer was determined to be 50(1)%,[29] while in $C(CH_2Br)_4$ at 413 K it is 58(2)%.[30] There appear to be no other measurements of the relative abundances of conformers of molecules of this type in the gas phase, although spectroscopic observations invariably confirm that the D_{2d} and S_4 conformers predominate. Thus, the rather limited data indicate that the D_{2d} form is usually energetically favored, but that the 2-fold multiplicity of the S_4 form results if roughly equal proportions, with the substituent X having surprisingly little influence on the balance.

A recent study of tetravinylmethane has interpreted gas electron diffraction data in terms of a single conformer of C_1 symmetry.[31] This resembles a molecule with

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Table 8. Symmetries and Average Bond Angles (deg) in Some $C(XY)_4$ Molecules with Distorted CX_4 Tetrahedral Structures

molecule	point group	⟨XCX	⟨XCX	method	ref
$C(OH)_4$	D_{2d}	103.6 × 2	112.5 × 4	B3LYP/6-311+G(2d,p)	34
	S_4	107.2 × 4	114.2 × 2	HF/3-21G*	35
$C(OMe)_4$	S_4	106.9 × 4	114.6 × 2	GED	36
$C(OC_6H_5)_4$	D_{2d}	101.0 × 2	114.0 × 4	X-ray, crystal	37
$C(OC_6H_3\text{-}Me_2\text{-}3,5)_4$	D_{2d}	101.3 × 2	114.3 × 4	X-ray, crystal	37
$C(CH_2OH)_4$	D_{2d}	106.7 × 2	110.9 × 4	X-ray, crystal	38
$C(SCF_3)_4$	S_4	106.0 × 4	116.6 × 2	GED	39
$C(SC_6H_5)_4$	S_4	106.3 × 4	116.0 × 2	X-ray, crystal	40
$B(OH)_4^-$	D_{2d}	106.2 × 2	111.1 × 4	B3LYP/6-311+G(2d,p)	34

S_4 symmetry, but with one of the vinyl groups twisted in the opposite direction. This is consistent with the structure of this molecule in the crystalline phase,[32] but it is possible that the assumption that all angles at the central carbon atom were regular tetrahedral may influence the interpretation. Calculations of the structure of the isoelectronic ion $B(CH{=}CH_2)_4^-$ at the MP2/6-31+G** level[33] strongly favor the S_4 conformation, with pronounced deviation from tetrahedral symmetry at the boron atom, and with the D_{2d} conformer being the second minimum on the potential surface.

Reliable experimental information about angles at the central carbon atoms in $C(CH_2X)_4$ molecules is even more sparse. In D_{2d} and S_4 forms, two of the six angles are by symmetry different from the other four. In $C(CH_2Br)_4$,[30] the deviations from the regular tetrahedral angle are not significant, being no more than 0.8(9)°. In the study of $C(CH_2Cl)_4$,[29] it was assumed that two angles in the D_{2d} conformer were less than 109.5° by the same amount that two angles in the S_4 conformer were greater than 109.5°. The deviation refined to 2.4(9)°, which is inconsistent with the quoted angles of 106.1° (D_{2d}) and 111.9° (S_4). However, the directions of the distortions are consistent with those calculated, and confirmed experimentally, for CEt_4. In this case, the two angles in the D_{2d} conformer are reduced by 2.9 to 106.6° (with the other four therefore 111.0°), while in the S_4 conformer two angles are increased by just 1.3°, to 110.8°. Experimental angles for some alkoxides $C(OR)_4$ and sulfur analogues, and computed angles for $C(OH)_4$ and $B(OH)_4^-$, are compiled in Table 8. In all cases the symmetry of the central MX_4 core is D_{2d} or S_4.

In the absence of extensive information about gas-phase molecules, we turned to crystallographic data for NEt_4^+ and BEt_4^-. There are more than 1000 published structures of NEt_4^+ ions, but in many the parameters for the ion are not sufficiently reliable. Selecting only organic compounds, with R factor < 0.05, $\sigma(C-C) < 0.5$ pm, and no disorder, just 12 independent ions, in 10 structures, remained. In 11 of these the ion had approximately D_{2d} symmetry, with two CNC angles in the range 105.3−107.3° (mean 106.4°). In the remaining example, the angles were 111.4 and 111.7°, and the ion symmetry was approximately S_4.[41] A much fuller analysis of NEt_4^+ structures, with more relaxed selection criteria, has been performed.[13] Of 208 ions, 163 had D_{2d} symmetry and 45 had S_4 symmetry. In the case of BEt_4^- there were no structures that even came close to meeting these stringent requirements, and just two that came within an acceptable range. In one of these[42] the ion has approximate S_4 symmetry, with two angles widened to 111.1 and 114.1°, and the other four in the range 106.3−109.5°. In the second structure there were two independent anions, each on a special position with S_4 symmetry, but in fact only very slightly distorted from D_{2d} local symmetry.[34] There were two small and four large angles in each of these, with the narrow angles being 107.9 and 107.1° in the two ions. The NEt_4^+ and BEt_4^- ions are thus very similar indeed to the isoelectronic CEt_4 molecule. Why are the angles distorted in this way?

In two papers[34,42] and a review[43] it was shown that the geometry of many molecules of the type AX_3 and AX_4, particularly those of Be, B, and C where X is a monatomic ligand such as F, Cl, or O^- or a linear ligand such as CN, can be understood on the basis that the ligands X are close-packed around the central atom. When there is more than one type of ligand X, then the geometry deviates from tetrahedral for AX_4 and equilateral triangular for AX_3 but the distances between any two given ligands are very nearly constant, independent of the coordination number and of the number of different ligands. For all ligands such as OX, NX_2, and CX_2Y a molecule with four equivalent ligands, such as $C(OH)_4$, has a geometry around the central atom A that is not tetrahedral. There are two different nontetrahedral bond angles, and the molecule has overall D_{2d} or S_4 symmetry. From an analysis of the calculated electron density distribution (B3LYP (6-311+(G2d,p))) by the AIM method,[43] it was shown that the electron distribution around monoatomic or linear ligands is cylindrically symmetrical as expected, but around other ligands such as OH and CH_2CH_3[44] it has a lower symmetry. The contact radius of such ligands varies with direction from the ligand, and close stacking of the ligands around the central atom is obtained in the S4 and D2d forms, leading to two different interligand distances and two corresponding bond angles.[34,44] This provides an alternative explanation for the nontetrahedral geometry to that provided by the conformational analysis based on molecular mechanics

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discussed in the Introduction. A full discussion of this model is in preparation.[44]

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Supporting Information Available: Listings of (a) absolute energies for the theoretical computations and (b) atomic coordinates for the theoretically optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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