Molecular Structure of 3,4-Dimethylenehexa-1,5-diene ([4]Dendralene), C$_8$H$_{10}$, in the Gas Phase As Determined by Electron Diffraction and *ab Initio* Calculations

Paul T. Brain, Bruce A. Smart, Heather E. Robertson, Martin J. Davis,[†]
David W. H. Rankin,* William J. Henry, and Ian Gosney

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.

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The molecular structure of 3,4-dimethylenehexa-1,5-diene ([4]dendralene), C$_8$H$_{10}$, has been determined in the gas phase. A single conformer with C_2 symmetry, having two almost planar, *anti* butadiene groups orientated with a dihedral angle C(2)C(3)C(4)C(5) of 71.7(19)°, is detected by electron diffraction employing flexible restraints derived from *ab initio* computations. Other experimental structural parameters (r_α/pm, $\angle_\alpha$/°) are: C(1)=C(2) 133.4(1), C(3)=C(7) (not in main chain) 134.0(1), C(2)−C(3) 147.4(2), C(3)−C(4) 149.6(3), C(1)C(2)C(3) 124.4(3), C(2)C(3)C(4) 119.2(5), C(4)C(3)C(7) 117.6(7), and C(7)C(3)C(2)C(1) −174.8(28). *Ab initio* computations at the MP2/6-311G* level predict that the vapor consists of *ca.* 90% of the conformer found experimentally, the other 10% comprising four other conformers.

Introduction

Cross-conjugated acyclic polyenes, otherwise known as dendralenes, are interesting compounds from a synthetic and a theoretical point of view.[1] As the simplest member of this class of compounds, [3]dendralene **1** (3-methyl-enepenta-1,4-diene) has been the subject of numerous theoretical studies,[2] but relatively little experimental work.[3] The molecular structure of **1** has been investigated by gas-phase electron diffraction (GED) to reveal an *anti,skew* conformation (Scheme 1) consisting of an *anti*-butadiene fragment with the other vinyl group subtending a dihedral angle of *ca.* 40° with the butadiene plane, rotated from the *syn* configuration.[4]

In the present paper, we report the results of a study of the molecular structure of [4]dendralene **2** (3,4-dimethylenehexa-1,5-diene) by GED and *ab initio* computations. *A priori*, [4]dendralene is a dehydrodimer of butadiene, having *two* overlapping cross-conjugated diene systems. Although **2** was first prepared in 1962,[5] details of its structure remain unknown, not least since it proved difficult to obtain in a pure state until 1985.[6] The similarity of the UV spectrum ($\lambda_{max} = 216.5$ nm)[5,7] to that of butadiene ($\lambda_{max} = 217$ nm) suggests that [4]dendralene may be regarded as two butadienyl groups bonded together without significant further cross conjugation.

† Present address: DFEI/SME, University of Cranfield, Cranfield, Beds., MK43 0AL, UK.
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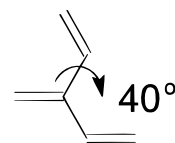(4) Almenningen, A.; Gatial, A.; Grace, D. S. B.; Hopf, H.; Klaeboe, P.; Lehrich, F.; Nielsen, C. J.; Powell, D. L.; Trætteberg, M. *Acta Chem. Scand.* **1988,** *A42,* 634.
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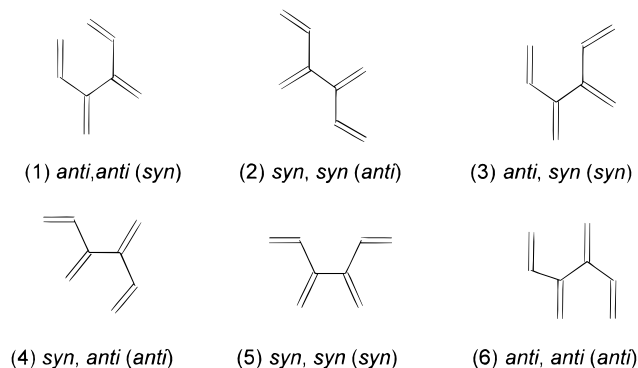(6) Buchan, C. M.; Cadogan, J. I. G.; Gosney, I.; Henry, W. J. *J. Chem. Soc., Chem. Commun.* **1985,** 1785.
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Scheme 1

Scheme 2

(1) *anti,anti (syn)*　　(2) *syn, syn (anti)*　　(3) *anti, syn (syn)*

(4) *syn, anti (anti)*　　(5) *syn, syn (syn)*　　(6) *anti, anti (anti)*

Different arrangements of the four double bonds give rise to six possible conformers, the planar forms of which are shown in Scheme 2. Each conformer, planar or nonplanar, is described by reference to the conformation of each butadiene, and to the orientation of the vinyl groups relative to one another. In this study, we have investigated the relative populations of these conformers and their distortions from the idealized structures of Scheme 2.

Experimental Section

Synthesis. [4]Dendralene was prepared by extrusion of SO$_2$ from 6,7-dimethylene-3-thiabicyclo[3.2.0]heptane-3,3-dioxide (**3**) under flash vacuum pyrolytic conditions at 823 K (Scheme 3).[6] The general technique and apparatus for flash vacuum pyrolysis have been described previously.[8]

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Table 1. Nozzle-to-Plate Distances, Weighting Functions, Correlation Parameters, Scale Factors and Electron Wavelengths

nozzle-to-plate 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}			
285.4	2	20	40	124	144	−0.1374	0.772(3)	5.686
128.3	4	40	60	280	336	−0.0901	0.781(7)	5.687

^{a} Figures in parentheses are the estimated standard deviations. ^{b} Determined by reference to the scattering pattern of benzene vapor.

Scheme 3
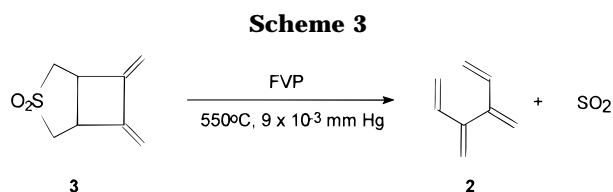
Typically, 0.155 g (0.900 mmol) of **3**,[6] admixed with galvi-noxyl to prevent polymerization, were pyrolyzed (inlet, 358 K; oven, 823 K) at 9×10^{-3} mmHg pressure. After *ca.* 90 min, all of the starting sulfone had evaporated and a colorless band had collected in the trap held at 77 K. After completion of the pyrolysis, the system was isolated from the pump and filled with nitrogen gas. Isolation of pure [4]dendralene **2** as a clear liquid (0.080 g, 83%) was achieved by removal of SO_2 from the crude product mixture by pumping on the trap warmed to 233 K at 0.05 mmHg pressure, followed by flash distillation, allowing the trap to warm to room temperature. The purity of the compound was checked by reference to the ^1H and ^{13}C NMR spectra of a CDCl$_3$ solution: ^1H NMR δ 6.43 (2H, dd, J = 17.30 and 10.50 Hz), 5.24 (2H, m), 5.18 (2H, d, J = 17.3 Hz), 5.10 (2H, d, J = 10.5 Hz), 5.05 (2H, m) and identical to data reported by Roth *et al.*[9] to whom we are indebted for providing a copy of the spectrum; ^{13}C(DEPT) NMR δ 137.30, 117.47 and 116.33.

Electron-Diffraction Measurements. Electron-scattering intensities were recorded on Kodak Electron Image plates using the Edinburgh gas-diffraction apparatus operating at *ca.* 44.5 kV (electron wavelength *ca.* 5.7 pm).[10] Nozzle-to-plate distances were *ca.* 128 and 285 mm, yielding data in the *s* range 20−336 nm^{-1}; four usable plates were obtained at each distance. The sample and nozzle were held at *ca.* 293 K during the exposure periods.

The scattering patterns of benzene were also recorded for the purpose of calibration; these were analyzed in exactly the same way as those of the [4]dendralene so as to minimize systematic errors in the wavelengths and camera distances. Nozzle-to-plate distances, weighting functions used to set up the off-diagonal weight matrix, correlation parameters, final scale factors, and electron wavelengths for the measurements are collected together in Table 1.

The electron-scattering patterns were converted into digital form using a computer-controlled Joyce-Loebl MDM6 microdensitometer with a scanning program described previously.[11] The programs used for data reduction[11] and least-squares refinement[12] have been described elsewhere; the complex scattering factors employed were those listed by Ross *et al.*[13]

Theoretical Calculations. A graded series of *ab initio* molecular-orbital calculations was undertaken to predict geometrical parameters and to obtain theoretical harmonic force fields. All calculations were carried out on a DEC Alpha APX

1000 workstation using the Gaussian suite of programs.[14] Geometry optimizations were performed using standard gradient techniques at the SCF level of theory using the 3-21G*,[15−17] 6-31G*,[18−20] and 6-311G*[21] basis sets. Subsequently, the two larger basis sets were adopted for calculations at the MP2-(FC) level of theory.

Vibrational frequency calculations were performed on all stationary points located at the SCF/3-21G* and SCF/6-31G* levels to verify structures as minima on the potential-energy surface (PES). In addition, a geometry optimization and frequency calculation were undertaken for the lowest-energy conformer using density-functional methods at the B3LYP/6-31G* level.[22] A fine grid containing 99 radial shells and 302 angular points per shell for each atom was used for these calculations.

Molecular Model

Several different models were used to generate the atomic coordinates of [4]dendralene employing the atom-numbering scheme shown in Figure 1. For a single conformer with C_2 symmetry, twelve geometrical parameters were used to define the molecular structure, as given in Table 2. These include five bond distances: the average of all C—C and C=C distances (p_1); the difference between the mean C—C and the mean C=C distances (p_2); the difference between the C—C distances (p_3); the difference between the C=C distances (p_4); and the mean of the three different C—H distances (p_5). For each distinct type of C—H distance, the difference from the mean was fixed at the theoretical value (MP2/6-31G* level). Assuming planarity of the atoms within the groups H(2)C(2)C(1)H$_2$ and C(2)C(3)C(7)H$_2$, the other parameters consisted of the C=C—H(1) angle (p_6), assumed equal for all C=C—H$_2$ groups; the vinylic C—C=C angle (p_7); the angle H(2)—C(2)=C(1); the torsion of the vinyl group about C(2)—C(3), *i.e.* the dihedral angle C(7)C(3)C(2)C(1), defined as 0° for a *syn* planar conformation (p_9); the angles C(4)—C(3)—C(2) (p_{10}) and C(4)—C-(3)=C(7) (p_{11}); and the orientation of one butadiene group
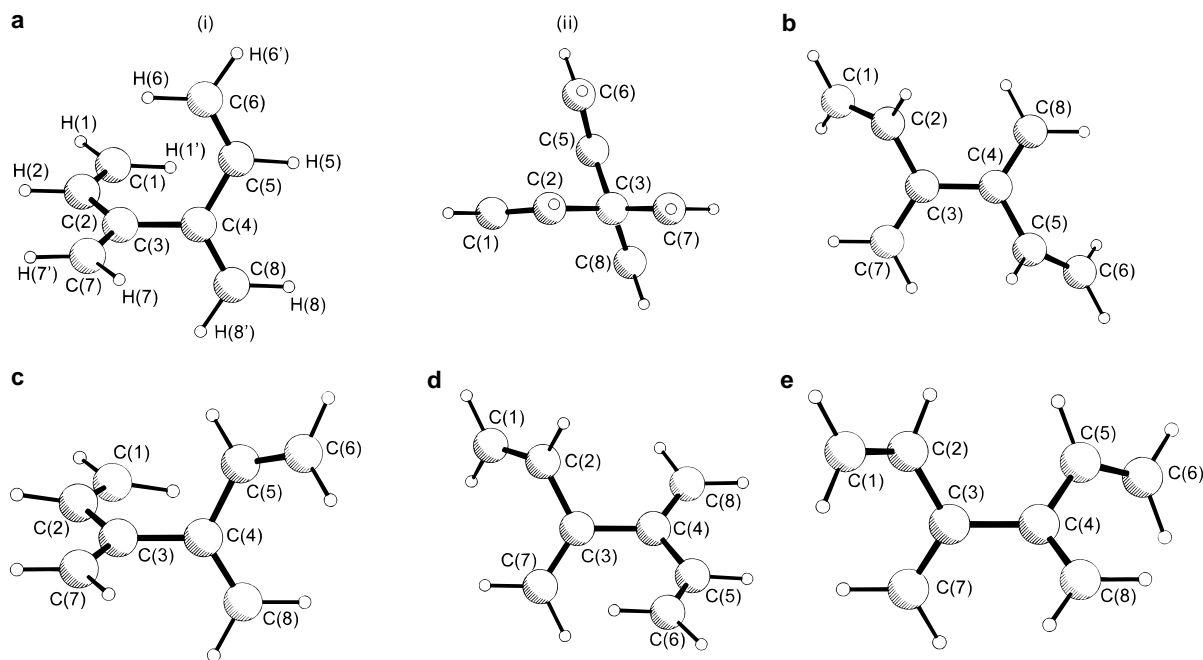
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Figure 1. Views of [4]dendralene: (a) conformer (1) in the optimum refinement of the electron-diffraction data: (i) perspective view, and (ii) view along C(3)–C(4); (b–e) perspective views of conformers (2–5), respectively, optimized at the MP2/6-311G* level of theory.

Table 2. Molecular Parameters (r_α° structure)

no.	parameter[a]	distance/pm or angle/°[b]
1	$1/7[rC(3)-C(4) + 2rC(2)-C(3) + 2rC(1)-C(2) + 2rC(3)-C(7)]$	139.87(4)
2	$1/3[rC(3)-C(4) + 2rC(2)-C(3)] - 1/2[rC(1)-C(2) + rC(3)-C(7)]$	14.4(1)
3	$rC(3)-C(4) - rC(2)-C(3)$	2.2(5)
4	$rC(3)-C(7) - rC(1)-C(2)$	0.5(3)
5	$1/5[2rC(1)-H(1) + rC(2)-H(2) + 2rC(7)-H(7)]$	109.1(1)
6	C(2)C(1)H(1)	119.4(4)
7	C(3)C(2)C(1)	124.4(3)
8	H(2)C(2)C(1)	121.4(7)
9	C(7)C(3)C(2)C(1)	−174.8(28)
10	C(4)C(3)C(2)	119.2(5)
11	C(4)C(3)C(7)	117.6(7)
12	C(2)C(3)C(4)C(5)	71.7(19)

[a] For atom-numbering scheme, see Figure 1. [b] Figures in parentheses are the estimated standard deviations.

relative to the other defined by the torsion angle C(2)—C(3)—C(4)—C(5) (p_{12}).

On the basis of the *ab initio* calculations detailed below, several other conformers are also expected to be present in small amounts (<10%) in the gas phase at room temperature. Thus, other models were employed which explored the possibility of contributions to the scattering by these conformers. Since the fraction of each of these conformers was predicted to be small, their geometrical parameters were not expected to be refinable. Thus, their structures were defined in terms of bond-distance and bond-angle differences, fixed relative to the predominant C_2 conformer, and fixed torsion angles; these angles and differences were fixed at the values computed *ab initio* (MP2/6-31G* level).

Results

Ab Initio Calculations. Each of the six possible conformers of [4]dendralene was considered for theoretical studies. Vibrational-frequency calculations performed at the SCF/3-21G* and SCF/6-31G* levels showed that conformers derived from the starting positions 1–5 in Scheme 2 all represent local minima on the PES. An extensive search of the surface at the SCF/3-21G*, SCF/

6-31G*, and MP2/6-31G* levels failed to locate a stationary point derived from starting position (6), *i.e. anti,anti* (*anti*); this arrangement was found always to collapse to a structure derived from starting position (1), *anti,anti* (*syn*).

The relative energies of the five local minima are presented in Table 3. At all levels, conformer (1) was found to be the lowest energy structure by at least 6.8 kJ mol^{-1}. The energy ordering of the conformers did not alter with improvements in the theoretical treatment except in the case of conformers (2) and (3), for which the energy separation was never more than 0.7 kJ mol^{-1} when the effects of zero-point energy are taken into consideration. At the highest level of theory available to us [MP2/6-311G* + 0.9·ZPE(SCF/6-31G*)], the energy ordering of the conformers is predicted to be (1) < (3) < (2) < (4) < (5). Neglecting entropy effects, and taking account of the two-fold degeneracy of conformers (3) and (4), this corresponds to an equilibrium mixture consisting of 89.1% (1), 5.7% (3), 2.6% (4) and 2.6% (2) [<0.1% (5)] in the gas phase at 293 K.

Selected geometrical parameters for the lowest energy conformer (1), optimized at several different theoretical levels, are reported in Table 4. Bond lengths were found to be fairly insensitive to the adopted theoretical method,

Table 3. Variation of Relative Energy (kJ mol⁻¹) and Proportion with *ab Initio* Level for Conformers of [4]Dendralene

level/basis set	relative energy^a (% at 293 K)				
	conformer (1)	conformer (2)	conformer (3)	conformer (4)	conformer (5)
SCF/3-21G*	0.0 (83.07)	7.46 (3.89)	6.79 (10.23)	9.97 (2.77)	18.94 (0.03)
SCF/6-31G*	0.0 (87.50)	7.90 (3.42)	7.96 (6.67)	10.46 (2.39)	20.20 (0.02)
MP2/6-31G*	0.0 (82.37)	6.86 (4.93)	7.48 (7.64)	8.50 (5.03)	19.33 (0.03)
SCF/6-311G*	0.0 (90.82)	8.90 (2.35)	8.55 (5.43)	11.90 (1.37)	21.01 (0.02)
MP2/6-311G*	0.0 (89.05)	8.63 (2.58)	8.37 (5.73)	10.27 (2.63)	21.47 (0.01)
ΔZPE (SCF/3-21G*)^b	0.00	0.42	−0.08	0.17	−1.07
ΔZPE (SCF/6-31G*)^b	0.00	0.71	0.00	0.62	−0.78

^{a} Corrected for zero-point energy scaled by 0.9; SCF/3-21G* corrected for ZPE(SCF/3-21G*) and all others for ZPE(SCF/6-31G*).
^{b} Unscaled. Relative to the ZPE for conformer (1).

Table 4. Variation of Structural Parameters (r/pm, ∠/°) with *ab Initio* Level for Conformer (1)

parameter^a	theoretical level/basis set (r_e)						expt ($r_\alpha°$) GED^b
	SCF/3-21G*	SCF/6-31G*	SCF/6-311G*	B3LYP/6-31G*	MP2/6-31G*	MP2/6-311G*	
C(2)—C(3)	147.8	147.9	147.9	147.1	146.8	147.0	147.4(2)
C(3)—C(4)	150.0	150.0	150.0	150.1	149.1	149.2	149.6(3)
C(1)=C(2)	131.9	132.2	132.1	133.9	134.4	134.5	133.4(1)
C(3)=C(7)	132.3	132.6	132.5	134.5	134.9	135.1	134.0(1)
C-H (mean)	107.3	107.6	107.6	108.7	108.7	108.6	109.1(1)
C=CH(H) (mean)	121.6	121.6	121.6	121.6	121.4	121.3	119.4(4)
C(3)C(2)C(1)	125.3	126.1	126.2	126.1	124.8	124.6	124.4(3)
H(2)C(2)C(1)	119.7	119.0	118.9	119.0	119.3	119.3	121.4(7)
C(7)C(3)C(2)C(1)	−174.3	−173.3	−174.1	−174.4	−172.4	−173.4	−174.8(28)
C(4)C(3)C(2)	118.4	119.3	119.3	119.5	119.1	118.9	119.2(5)
C(4)C(3)C(7)	120.5	120.5	120.5	120.2	120.1	120.1	117.6(7)
C(2)C(3)C(4)C(5)	80.2	77.8	79.1	76.3	73.8	74.0	71.7(19)
energy/Hartrees	−306.9652454	−308.6819625	−308.7389645	−310.786397	−309.6927315	−309.8006391	−

^{a} For atom-numbering scheme, see Figure 1. ^{b} Figures in parentheses are the estimated standard deviations.

Table 5. Theoretical (MP2/6-311G* level) Structural Parameters (r/pm, ∠/°) for Conformers of [4]Dendralene^a

parameter^b	conformer (1) (C_2) a,a (s)	conformer (2) (C_2) s,s (a)	conformer (3) (C_1)^c a,s (s)	conformer (4) (C_1)^c s,a (a)	conformer (5) (C_2) s,s (s)
C(2)—C(3)	147.0	147.9	147.5	147.6	147.9
C(3)—C(4)	149.2	148.2	149.1	149.0	149.1
C(1)=C(2)	134.5	134.4	134.5	134.5	134.4
C(3)=C(7)	135.1	135.3	135.0	135.3	134.9
C—H (mean)	108.6	108.6	108.6	108.6	108.6
C=CH(H) (mean)	121.3	121.2	121.2	121.2	121.1
C(3)C(2)C(1)	124.6	123.5	124.1	125.1	123.4
H(2)C(2)C(1)	119.3	119.6	119.4	119.1	118.8
C(7)C(3)C(2)C(1)	−173.4	−48.5	−168.3	−45.2	45.6
C(8)C(4)C(5)C(6)	−173.4	−48.5	−39.7	164.5	45.6
C(4)C(3)C(2)	118.9	118.0	117.3	118.8	117.9
C(4)C(3)C(7)	120.1	121.2	120.7	120.7	120.6
C(2)C(3)C(4)C(5)	74.0	158.4	69.5	137.8	−56.4
energy/Hartrees	−309.8006391	−309.7975954	−309.7974499	−309.7969414	−309.7921958
rel energy^d/kJ mol⁻¹	0.00	8.63	8.37	10.27	21.47
% at 293 K	89.05	2.58	5.73	2.63	0.01

^{a} Key: a = *anti*, s = *syn*. ^{b} For atom-numbering scheme, see Figure 1. ^{c} Mean value as for C_2 symmetry. ^{d} Corrected for zero-point energy (SCF/6-31G* scaled by 0.9).

generally varying over a range of less than 1 pm with different basis sets. For example, C(3)=C(7) changes from 132.3 to 132.6 to 132.5 pm for the SCF calculations employing the 3-21G*, 6-31G*, and 6-311G* basis sets, respectively. The introduction of electron correlation leads to the expected lengthening of the C=C bonds by *ca.* 2 pm.[23] Bond and dihedral angles were consistent to 1−2°, except for the C(2)C(3)C(4)C(5) dihedral angle which was reduced from *ca.* 79° to *ca.* 74° when the effects of electron correlation were taken into consideration at the MP2 level.

Variations in the geometrical parameters of each of the four conformers (2−5) with theoretical level exhibit the same general trends as observed for conformer (1), and are not detailed here. Structural parameters for conformers (2−5) at the MP2/6-311G* level are presented in Table 5.

GED Refinement. The $r_\alpha°$ structure of [4]dendralene was refined. For each conformer (1−5), a harmonic vibrational force field was computed at the HF/6-31G* level, and the Cartesian force constants were transformed into those described by a set of symmetry coordinates using the program ASYM40.[24] As a full analysis of experimental vibrational frequencies is not available for the compound, it was not possible to scale the theoretical force constants on this basis. Instead, as the best

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(24) ASYM40 is an updated version of ASYM20: Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

alternative, empirical scale factors were employed, based on the work of Pulay *et al.* for butadiene:[25] 0.87 for C—H and C=C bond stretches, 0.92 for C—C bond stretches, and 0.80 for angle bends and torsions. Values for the root-mean-square amplitudes of vibration (u) and perpendicular amplitude corrections (K) were then derived from the scaled force constants using ASYM40.[24]

Initial refinements of the electron-diffraction pattern assumed the presence of a single conformer with C_2 symmetry, for which starting values of geometrical parameters were taken from the structure of conformer (1) optimized *ab initio* at the MP2/6-31G* level. It was possible to refine nine of the twelve geometrical parameters (Table 2); introduction of parameters defining differences between the C—C and C=C bond lengths, *i.e.* p_3 and p_4, and of p_8, the angle H(2)C(1)C(2), either caused the refinement to become unstable (large oscillations in the R_G factor between cycles) or led such parameters to adopt unrealistic values. These parameters were refined subsequently using flexible restraints.

Flexible restraints may allow the refinement of parameters which would otherwise have to be fixed.[26] Estimates of the values of these restrained quantities and their uncertainties are used as additional observations in a combined analysis similar to those routinely carried out for electron-diffraction data combined with rotation constants and/or dipolar coupling constants.[27] The values and uncertainties for the extra observations are derived from another method such as X-ray diffraction or theoretical computations. *All* geometrical parameters are then included in the refinements. In cases where a restrained parameter is also a refinable parameter, if the intensity pattern contains useful information concerning the parameter, it will refine with an esd less than the uncertainty in the corresponding additional observation. However, if there is essentially no relevant information, the parameter will refine with an esd equal to the uncertainty of the extra observation and its refined value will equal that of the restraint. In this case, the parameter can simply be fixed, in the knowledge that doing this does not influence either the magnitudes or the esds of other parameters. In some cases, because increasing the number of refining parameters allows all effects of correlation to be considered, some esds may increase. Overall, this approach utilizes all available data as fully as possible and returns more realistic esds for refining parameters; the unknown effects of correlation with otherwise fixed parameters are revealed and included.

Using flexible restraints, it was possible to refine p_3, p_4, and p_8. These were restrained directly with values $p_3 = 2.3 \pm 0.5$ pm, $p_4 = 0.50 \pm 0.25$ pm, and $p_8 = 119.3 \pm 2.0°$.

In addition, eighteen amplitudes of vibration were included in the final refinements, of which seven (C···H distances > 300 pm) were refined using restraints. For amplitudes tied together, the ratio of amplitudes within each group was fixed at the theoretical value.

(25) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037.

(26) (a) Blake, A. J.; Brain, P. T.; McNab, H.; Miller, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A. *J. Phys. Chem.* **1996**, *100*, 12280. (b) Brain, P. T.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1996**, 4589.

(27) For example, see: Abdo, B. T.; Alberts, I. L.; Attfield, C. J.; Banks, R. E.; Blake, A. J.; Brain, P. T.; Cox, A. P.; Pulham, C. R.; Rankin, D. W. H.; Robertson, R. E.; Murtagh, V.; Heppeler, A.; Morrison, C. *J. Am. Chem. Soc.* **1996**, *118*, 209.

Table 6. Interatomic Distances (r_a/pm) and Amplitudes of Vibration (u/pm)

no.	atom pair[a,b]	distance[c]	amplitude[c]
1	C(2)—C(3)	147.8(2)	5.1(1)
2	C(3)—C(4)	149.7(3)	5.2 (tied to u_1)
3	C(1)=C(2)	134.9(1)	} 4.4 (1)
4	C(3)=C(7)	134.6(1)	
5	C(7)—H(7)	110.7(1)	
6	C(7)—H(7′)	110.6(1)	
7	C(2)—H(2)	112.6(1)	} 8.3(1)
8	C(1)—H(1′)	112.6(1)	
9	C(1)—H(1)	110.8(1)	
10	C···H (two-bond)	211.0(4)−219.2(19)	10.0−10.5(2)
11	C(3)···C(8)	242.9(8)	6.6(4)
12	C(2)···C(7)	248.2(5)	6.4
13	C(1)···C(3)	248.7(4)	6.3 } (tied to u_{11})
14	C(2)···C(4)	256.3(7)	6.9
15	C(1)···C(4)	296.3(16)	11.7(13)
16	C(7)···C(8)	306.9(23)	11.4 (tied to u_{15})
17	C(2)···C(5)	329.5(22)	12.5 (tied to u_{18})
18	C(1)···C(5)	339.1(23)	16.6(20)
19	C(2)···C(8)	347.2(16)	12.5(14)
20	C(1)···C(6)	352.4(48)	18.2 (tied to u_{19})
21	C(1)···C(7)	370.1(4)	7.0(4)
22	C(1)···C(8)	376.2(31)	21.4(41)
23	C···H (three/four-bond)	259.7−272.9	15.6−21.0(14)[d]
24	C···H (three-bond)	343.9−352.8	10.1−10.7(10)[d]
25	C···H (four-bond)	402.7−408.2	13.6−15.4(12)[d]

[a] For atom-numbering scheme, see Figure 1. [b] Other C···H and H···H nonbonded distances were included in the refinements but are not listed here. [c] Values in parentheses are the estimated standard deviations. [d] Refined as a group; one amplitude refining with others having a fixed ratio relative to it.

A careful study of models defining more than one conformer was undertaken. For each, the change in the R_G factor was followed as a function of the composition of the mixture. For all compositions, the R_G factor was found to be greater than that for the single conformer alone, *i.e.* no other minima were located on the R_G *vs* % composition surface generated. At the 95% confidence level,[28] the gas-phase sample of [4]dendralene was found experimentally to consist of 100 ± 2% of conformer (1).

Values of the principal interatomic distances for the final refinement ($R_G = 0.019$, $R_D = 0.021$) are listed in Table 6 and the most significant values of the least-squares correlation matrix are given in Table 7. The experimental and difference radial-distribution curves are shown in Figure 2 and the molecular-scattering intensities in Figure 3. Cartesian coordinates are included as part of the Supporting Information.

Discussion

In the gas phase at 293 K, [4]dendralene is found experimentally by electron diffraction to consist of a single conformer with C_2 symmetry (Figure 1a). The butadiene groups, which are twisted by 5.2(28)° from a perfectly planar conformation, have *anti* arrangements of the C=C bonds. They are orientated at 71.9(19)° to one another relative to the *anti,anti* (*syn*) starting position in Scheme 2.

The principal structural parameters predicted by the *ab initio* computations are given in Table 4. At the MP2/6-311G* level, the values defining the equilibrium geometry (r_e) for conformer (1) are in very good agreement with those refined from the electron-diffraction pattern ($r_\alpha°$). Four other minima, apart from that observed experimentally, were located on the PES; relative energies at a range of theoretical levels are shown in Table

(28) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

Table 7.   Least-squares Correlation Matrix ($\times$ 100)^a

p_6	p_7	p_{10}	p_{11}	p_{12}	u_3	u_{11}	u_{15}	u_{18}	u_{22}	u_{23}	u_{24}	u_{25}	k_1	k_2	
-54															p_1
	64														p_6
		61				-54	59								p_7
			-63				-58				51				p_9
				-77		-90	76			53					p_{10}
						89	-76								p_{11}
								83				-65			p_{12}
				75											u_1
													50	55	u_3
							-78								u_{11}
										82					u_{15}
												-50			u_{18}
											73	-52			u_{19}
														51	k_1

^{a} Only elements with absolute values $\geq$ 50 are shown. k_1 and k_2 are scale factors.
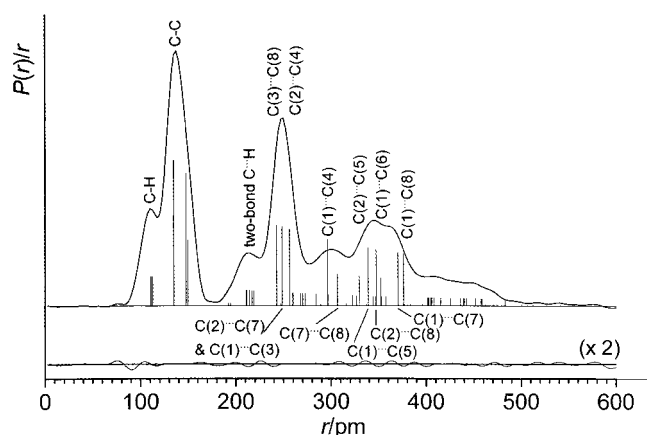
Figure 2. Observed and final weighted difference radial-distribution curves for [4]dendralene, conformer (1). Before Fourier inversion the data were multiplied by s exp[($-0.00002s^2$)/($Z_C - f_C$)($Z_C - f_C$)].
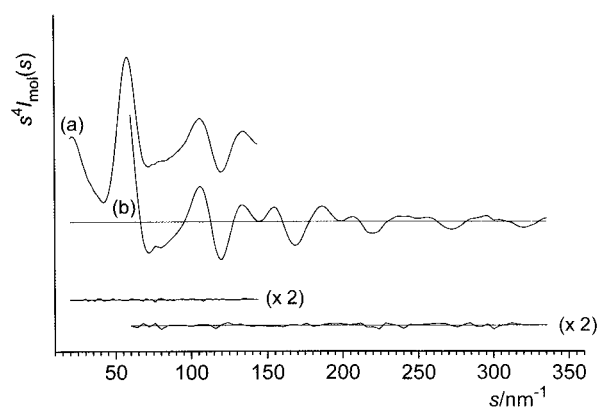
Figure 3. Observed and final weighted difference molecular-scattering intensity curves for [4]dendralene, conformer (1). Nozzle-to-plate distances were (a) 285, and (b) 128 mm.

3. At the MP2/6-311G* level, none of these additional conformers is predicted to constitute more than 6% of the gas-phase mixture. Such small proportions, coupled with the very similar interatomic-distance distribution, are consistent with these conformers not being detected experimentally by electron diffraction.

The details of the structures of conformers (2−5) optimized at the MP2/6-311G* level are given in Table 5 and illustrated in Figure 1. Conformers (1) and (3) and conformers (2) and (4) may be viewed as pairs in that each constitutes a reduction in symmetry from C_2 to C_1 brought about by changing one butadiene group from *anti* to *syn*, or vice versa, while retaining the relative orientation of the butadienes, *e.g.* for conformers (1) and (3), *a*, *a* (*s*) → *a*, *s* (*s*). Similarly, conformers (5) and (2) are related in that they have *syn* conformations for the butadienes but different relative orientations of these groups.

With the exception of conformer (1), all the conformers show large deviations from perfect *anti* and, more particularly, perfect *syn* conformations of one or both of the butadienyl groups. For example, in conformer (2) the deviation is 48.5° from *syn* [C(7)C(3)C(2)C(1)], and in conformer(3) the deviation is 11.7° from *anti* [C(7)C(3)C-(2)C(1)] and 39.7° from *syn* [C(8)C(4)C(5)C(6)]. The level of conjugation within each butadienyl group is thus variable, decreasing with increased distortion of the conformation. For conformers (2−5) the distortions are greater than for conformer (1) and all have slightly longer C(2)−C(3) distances, as expected.

Notwithstanding the dihedral angles, the bond lengths and angles describing the five conformers are very similar, indicative of steric factors (C$\cdots$C, C$\cdots$H, and H$\cdots$H nonbonded interactions) being responsible predominantly for the disposition of the groups in each. Cross conjugation of the butadiene groups would be evidenced by a shortening of C(3)−C(4) relative to C(2)−C(3) and expected only for dihedral angles C(2)C(3)C(4)C-(5) approaching 0° or 180°. Of the five conformers, conformer (2) offers the best approximation to this criterion, with C(2)C(3)C(4)C(5) = 158.4°, and conformer (1) the worst, with C(2)C(3)C(4)C(5) = 74°. Conformer (2) demonstrates the smallest C−C difference (0.3 pm) [it has the shortest C(3)−C(4) bond length (148.2 pm)], and conformer (1) the largest (2.2 pm) [it has the longest C(3)−C(4) bond length (149.2 pm)], consistent with a π-bonding contribution to C(3)−C(4) in conformer (2). The UV spectrum of [4]dendralene, whether consisting predominantly (*ab initio*) or completely (GED) of conformer (1), would thus be expected to be similar to that of butadiene, as is found experimentally (λ_{max} = 216.5 nm; *cf.* butadiene λ_{max} = 217 nm).[5,7]

[4]Dendralene may be considered as a 2-substituted *anti* butadiene (Table 8); structural parameters of related compounds are given in Table 8. On replacement of H at C(2) in butadiene,[29] the C=C−C *ipso* angle narrows and the other C−C=C angle widens, except for X = C(=CH$_2$)CH=CH$_2$, [4]dendralene, where it is unchanged. This is consistent with increased steric repulsions relative to butadiene on substitution; such interactions are presumably less marked for [4]dendralene where the near planar butadiene groups lie almost orthogonal to one another [C(2)C(3)C(4)C(5) = 71.7(19)°]. The attenuation of the C−C bond on substitution with particularly bulky groups, *i.e.* CH=CH$_2$,[4] C(=CH$_2$)CH=CH$_2$ and ^{t}Bu,[31] lends further support to the premise that nonbonded repul-

(29) Kveseth, K.; Seip, R.; Kohl, D. *Acta Chem. Scand.* **1980**, *A34*, 31.

Table 8. GED Structural Parameters (r_a) for Some 2-Substituted *Anti* Butadienes[a]

X	r(C=C)[b]	r(C-C)	∠C=C—C (*ipso*)	∠C—C=C	ref
H	134.9(1)	146.7(2)	124.4(1)	124.4(1)	29
CH$_3$	134.0(1)	146.3(2)	121.4(3)	127.3(3)	30
CH=CH$_2$	134.4(19)	147.9(3)	118.7(27)	126.6(31)	4
C(=CH$_2$)CH=CH$_2$	134.8(1)	148.4(2)	123.2(4)	124.4(3)	this work
^{t}Bu	134.5(3)	148.5(10)	121.7(12)	126.2(12)	31
Cl[c]	134.2(2)	146.9(3)	123.5(1)	125.6(2)	32

[a] Values in parentheses are the estimated standard deviations. [b] Where two different C=C distances have been refined, a mean value is shown. [c] Combined GED/microwave analysis.

sions, rather than electronic factors, account primarily for the conformations of these compounds.[31,33]

Supporting Information Available: Listings of (a) absolute energies for the theoretical computations and (b) atomic coordinates for the GED and theoretically optimized geometries (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO962091H

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