A Reappraisal of the Structure of the Second Stable Conformer of Buta-1,3-diene

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The structure of the second stable conformer of buta-1,3-diene was investigated by computing the torsional frequencies and the resulting variation of the heat capacity with temperature (220—320 K) from potential energy curves based (a) on calorimetric and spectroscopic data and (b) on a comprehensive set of *ab initio* calculations. In general, there was good agreement between the *ab initio* predictions and the experimental frequencies localized in the *trans*-well. However, the *ab initio* values for the torsional frequencies localized in the second well, and the temperature variation of $C_p°$ based on the potential curves derived from the spectroscopic data, did not support the assignment of frequencies observed at 271.1 and 263.9 cm^{-1} to the second stable form. A new potential energy curve is proposed, which is in better agreement with the predictions of the *ab initio* calculations, and which accounts very well for the observed spectra and temperature variation of $C_p°$.

THE shape of the potential energy curve for rotation about the formal C–C single bond in buta-1,3-diene has been the subject of many experimental[1-4] and *ab initio* theoretical[5-11] investigations. All these studies have shown the most stable form to be the planar *trans*-conformation, in accord with several independent electron diffraction analyses.[12-14,†] There is, however, considerable disagreement as to whether the second slightly less stable form has a planar *cis*-structure or a nonplanar *gauche*-structure. There is also lack of agreement as to the precise position and height of the peak in the potential curve separating the two conformers. Values for its position range from *ca.* 70 to 95° (with the *trans*-conformer taken as 0°), and from *ca.* 5.0 to 7.6 kcal mol^{-1} for the barrier height.[1-11]

An accurate determination of the potential curve is important since it is the simplest case of rotation about a formal single bond in an acyclic conjugated structure, and thus serves as the model for semiempirical SCF–MO and empirical consistent force field calculations for more complicated structures of this kind. Furthermore, the height of the peak is important within the context of the homodesmotic reaction approach to the evaluation of delocalization energies for conjugated and aromatic hydrocarbons.[19-21] 90°-Buta-1,3-diene is utilized as a reference structure in which stabilization by overlap of adjacent *p*-lobes across the central formal single bond is reduced to a minimum, and an accurate assessment of peak height and position is essential to get its heat of formation which is needed in the calculations.

Unfortunately, however, each determination of the torsional potential curve for butadiene has, of necessity, involved certain assumptions and/or approximations.

(1) Aston *et al.*[1a] employed a statistical mechanical model to calculate the entropy, specific heat, and change of specific heat with temperature. By adjusting the height and position of the barrier and the torsional frequency (which was not accurately known at that time) they obtained a good fit for all three experimental quantities.[22] Two notable assumptions were made: (i) the second stable form was *assumed* to be *cis*, and (ii) the bond lengths and angles of this *cis* form were *assumed* to be the same as for the *trans*-form (*i.e.* a rigid rotation model was adopted). Furthermore, some of the vibrational frequencies employed by these authors differ from current assignments by up to 500 cm^{-1}.[1c,23]

(2) Carreira,[3] more recently, measured the torsional frequencies using a laser Raman technique, some of which had been observed earlier by Cole *et al.*[24] Although this was a crucial experiment which has clarified the shape of the potential well near 0° (*trans*), it has unfortunately led to further confusion regarding the nature of the second stable form. The difficulty is that the progression of observed torsional peaks appears to be interrupted at *ca.* 280 cm^{-1}. This requires an assignment of the peaks observed at 271.1, 263.9, and 256.7 cm^{-1} to either the *trans*-conformer or to the second less stable form, either *cis* or *gauche*. Carriera *chose* the *cis*-form and, using a computer program based on that of Lewis *et al.*,[25] showed that the observed spectrum could be adequately accounted for. However, an assumption had to be made. To use the Lewis *et al.* program it is necessary to choose a model for the change in bond lengths and angles during the rotation. Carreira adopted Allinger's molecular mechanics model,[26] which entails a change in the C–C formal single bond length from 1.468 Å in the *trans*-position to 1.518 Å in the 90° position, and to 1.471 Å at 180°. However, such a large increase of 0.050 Å from the *trans* to the 90° position is not supported by the *ab initio* studies of Skaarup *et al.*[10] or Altmann *et al.*,[11] who find the increase to be only 0.021—0.022 Å. Durig *et al.*[4] have recently questioned this structural model. They re-evaluated the potential curve using Carreira's spectroscopic data and the Lewis *et al.* program but assumed a model in which the formal single bond length *decreases* with rotation away from the

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† This is contrary to some semiempirical calculations in which the *cis*- or *gauche*-form was found to be the more stable.[15,16] Furthermore, Sudgen *et al.*[17] have argued on the basis of their observation of a low ionization potential that at room temperature a considerable portion of buta-1,3-diene exists in the *cis*-form. Recent measurements by Watanabe [18] have not confirmed their result.

trans position. This model was based on experimental structural data on glyoxal which suggests that the central single bond is shorter in the *cis*- than in the *trans*-form.[12,27] This is not likely to be true for buta-1,3-diene.[10] Durig *et al.* assigned the peaks below 280 cm^{-1} first to a *cis*-well and then to a *gauche*-well, and obtained excellent agreement with experiment in both cases, even though the curves differ substantially from each other and from that of Carreira. Unfortunately their calculation of the reduced moment of inertia was in error [28] which casts some doubt on their conclusions.

(3) Recently Compton *et al.*[1c] re-evaluated the work of Aston *et al.*[1a] considering the possibility of a *gauche*- as well as a *cis*-conformation. They found the energy difference between the *trans*- and the *gauche*- and *cis*-conformers to be 2.71 and 2.48 kcal mol^{-1} respectively, and concluded the second conformer was *cis* since the value of 2.48 kcal mol^{-1} is in better agreement with the value of 2.50 kcal mol^{-1} obtained by Carreira.[3] But this *assumes* the Carreira choice of a *cis*-well is correct and is *not* an independent check of the validity of this choice. Furthermore, if the Durig *et al.*[4] assignment of the frequencies at 271.1, 263.9, and 256.7 cm^{-1} to a *gauche*-well is correct, the *trans* – *gauche* energy difference is found to be 2.76 kcal mol^{-1}, in better agreement with the higher (*gauche*) value of Compton *et al.*[1c]

TABLE 1

C–C Bond lengths and $\widehat{\text{CCC}}$ angles in the three model structures used to study the rotation about the central C–C bond in buta-1,3-diene

	Rigid rotation model [a,b]			Adjusted model based upon *ab initio* calculations [c]			Molecular mechanics model [d]		
	trans	90°	180°	*trans*	90°	180°	*trans*	90°	180°
C–C(Å)	1.463	1.463	1.463	1.463	1.484	1.473	1.468	1.518	1.471
C=C(Å)	1.342	1.342	1.342	1.342	1.338	1.342	1.346	1.336	1.346
$\widehat{\text{CCC}}$(°)	123.6	123.6	123.6	123.6	123.3	125.9	122.3	120.7	125.7

[a] All C–H bond lengths taken as 1.093 Å, and $\widehat{\text{CCH}}$ angles as 120.9°.[12] [b] This geometry is close to that obtained in the electron diffraction study,[12] and was used in all cases of *rigid* rotation considered in this paper. [c] Based upon the results of Skaarup *et al.*,[10] with adjustments to bring them more in line with the experimental values, see text. In their notation in the *trans*-conformer r(C–H) = 1.094, r(C–H′) = 1.091, r(C–H″) = 1.093 Å, $\widehat{\text{CCH}}$ = 119.6, $\widehat{\text{CCH}'}$ = 121.8, and $\widehat{\text{CCH}''}$ = 121.8°. The variation of these bond lengths and angles as a function of the angle of rotation was also taken from this reference. [d] These results, obtained from the molecular mechanics program of Allinger *et al.*[26] were kindly supplied to us by Dr. L. A. Carreira.

(4) With regard to the theoretical studies, the *ab initio* potential energy curves of Dumbacher,[9] Pincelli *et al.*,[8] Skancke *et al.*,[7] Radom *et al.*,[6] and Skaarup *et al.*[10] were all obtained using relatively small basis sets (s and p functions only). Furthermore, either rigid rotation was assumed or only partial flexibility allowed (see, however, ref. 10). In addition electron correlation was either neglected or only partially included.

The purpose of this paper is four-fold. First, we assess the torsional potential curves proposed in the literature by computing the torsional frequencies and the resulting variation of heat capacity with temperature using a simple statistical mechanical model. Secondly, we repeat the calculations of Durig *et al.* using a geometry based on *ab initio* calculations. Thirdly, we investigate the importance of the choice of a specific model for the relaxation of bond lengths and angles during the rotation. Finally, we discuss the possibility that the frequencies observed at 271.1, 263.9, and 256.7 cm^{-1} may be due to higher level transitions within the *trans*-well and not to transitions belonging to the second stable form.

RESULTS

A *Potential Curves and Spectroscopic Data*.—In Table 1, we list values for the C–C bond lengths and $\widehat{\text{CCC}}$ angles in *trans*-, 90°-, and *cis*-buta-1,3-diene for the three models which will be used to study the torsional twist about the central C–C bond. Rigid rotation retaining the experimental geometry of the *trans*-conformer [12] on the one hand, and rotation of the flexible structure derived from the molecular mechanics program of Allinger *et al.*[26] on the other hand, represent two extremes with respect to the increase in length of the central C–C bond. In going from the *trans*- to the 90°-position the rigid rotation model assumes no change, whereas the molecular mechanics model predicts a large increase of 0.050 Å. To allow some variation in bond length and angle, but not to the extent of the molecular mechanics model, we have also considered a less flexible model based upon the recent *ab initio* geometry optimization by Skaarup *et al.*[10] using a (7,3) basis set contracted to ⟨5,3⟩ as ⟨3,1,1,1,1; 1,1,1⟩. However, like other *ab initio* calculations which use relatively small basis sets and neglect electron correlation, there are significant discrepancies between calculated and experimental values for the *trans*-conformer. For example, the formal C=C double bond length was found to be only 1.320 Å, *ca.* 0.022 Å too short. A similar discrepancy has been found with other basis sets for polyene structures.[29-33,*] We have, therefore, made adjustments to get a more realistic geometry for the less flexible structure (see Table 1).[†] No claim is made that this model is more 'correct' than that of Allinger. It is more flexible than a rigid rotation model, but less flexible than Allinger's model, so it is less likely to prejudice our conclusions.

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[*] To be assured that an increment of 0.022 Å is appropriate for the formal double bond with this particular basis set, a complete geometry optimization was carried out on ethylene using the MOLPRO program of Pulay.[34] The C=C bond length was found to be 1.315 Å, which when incremented by 0.022 Å yields 1.337 Å in excellent agreement with the experimental values of 1.335 [35] and 1.336 Å.[36]

[†] In the following text we shall refer to this model as the 'adjusted *ab initio* model'.

TABLE 2

$F(\phi)$ Values (A) and their Fourier decomposition (B) for the models in Table 1

	ϕ (°)	Rigid rotation model	Adjusted *ab initio* model [a]	Molecular mechanics model
(A)	0	2.68	2.68	2.63
	30	2.68	(2.67) [b]	2.61
	60	2.71		2.60
	90	2.85	2.85	2.70
	120	3.20		3.04
	(140)		3.60	
	150	3.73		3.80
	180	4.04	4.28	4.26
(B)	F_0	3.088	3.123	3.030
	F_1	−0.611	−0.681	−0.687
	F_2	0.253	0.315	0.375
	F_3	−0.063	−0.119	−0.127
	F_4	0.017	0.042	0.039
	F_5	−0.005		
	F_6	0.001		

[a] Skaarup *et al.*[10] only reported values at 0, 90, 140, and 180°.
[b] Although Skaarup *et al.* gave no value for 30°, we have included an estimated value of 2.67 in the analysis of $F(\phi)$ to flatten out the region near 0°, which is a characteristic feature of both the rigid rotation and the molecular mechanics model.

To compute the energy levels and wavefunctions in the various potential wells, the curves were expressed by equation (1) with the torsional angle $\phi = 0$ corresponding to the more stable *trans*-form, and with the values of N

$$V(\phi) = \sum_{n=1}^{N} Vn(1 - \cos n\phi)/2 \qquad (1)$$

ranging from 3 to 6. The Hamiltonian operator then takes the form (2) where $F(\phi) = h/4\pi CI_r(\phi)$ and $I_r(\phi)$ is the

$$H = -\frac{d}{d\phi} F(\phi) \frac{d}{d\phi} + V(\phi) \qquad (2)$$

reduced moment of inertia as defined by Pitzer.[37] The F values at several angles for the three models in Table 1 are listed in Table 2. Since F changes significantly, even for rigid rotation, it has been represented by the usual cosine series (3) where F_n takes the values given in section B of

$$F(\phi) = F_0 + \sum_{n} F_n \cos n\phi \qquad (3)$$

Table 2. As expected, the shape of the $F(\phi)$ function varies from one model to another, reflecting the differing degrees of stiffness during the rotation. It is quite striking how relatively insensitive $F(\phi)$ is to the torsional twist for the molecular mechanics model in the region 0—90°. This is primarily a consequence of the rapid onset and large change in the length of the central C–C bond which is characteristic of this model.

A computer program based on that of Lewis *et al.*[25] was written to calculate the energy levels and wavefunctions associated with the above Hamiltonian. 50 Sine and 50 cosine functions were used in each calculation.

Table 3 summarizes our designation of the various potential curves and some of their important characteristics. Table 4 gives the decomposition of $V(\phi)$ from equation (1). It may be noted that although the details vary widely, there is general agreement that V_1 is positive, V_2 is positive, and the largest value as would be expected, V_3 is positive and *not* negligible, and V_4 and V_6 are negative. In Table 5, we list the experimental and calculated spectroscopic transitions for $\Delta v = 2$ localized within the *trans*-portion of the well. The geometrical model used to compute $F(\phi)$ was that employed by the original author(s), but in several cases a second model was used to calculate the energy levels, *i.e.* the potential curve was left unaltered, but $F(\phi)$ in equation (2) was modified in order to test the sensitivity of the computed frequencies to this particular parameter. The following points may be noted.

(1) The transitions calculated *ab initio*, PCL1, PCL2, and SB are at least 10 cm^{-1} (3%), but usually $<$20 cm^{-1} (7%), greater than the observed values. But since the total molecular energy is still *ca.* 0.3—0.5 atomic units above the estimated Hartree–Fock (HF) limit,[38] small discrepancies of this magnitude are not unexpected. The Radom and Pople (RP) calculation (STO-3G) is never more than 4 cm^{-1} (1%) above the experimental values even though its predicted energy is nearly 2.0 atomic units above the HF limit.

(2) The only *ab initio* calculation which includes complete geometry optimization, SBS, leads to values that are in worse agreement with experiment. However, the reason may be in part that Skaarup *et al.*[10] only obtained four points on the potential curve, none of which was between 0 and 90°. As a consequence our Fourier analysis may be giving an imperfect representation of the actual curve in this

TABLE 3

Summary data from the various torsional potential curves for buta-1,3-diene

	Designation	Reference	Experimental (E) or theoretical (T)	Rotational model [a]	Second stable form	Barrier height (cm^{-1})	Energy difference (*trans*-second stable form) (cm^{-1})
A	Theoretical						
	PCL1	8	T [b] (*ab initio*, SCF)	R	*gauche*	2 496	908
	SB	7	T [b] (*ab initio*, *SCF*)	R	*gauche*	2 340	1 179
	SBS	10	T [b] (*ab initio*, SCF)	O	*gauche*	2 231 [c]	1 001 [c]
	PCL2	8	T [b] (*ab initio*, SCF + CI)	R	*gauche*	2 314	585
	RP	6	T [b] (*ab initio*, SCF)	R	*gauche*	2 311	917
B	Experimental						
	C	3	E (Spectroscopic)	MM	*cis*	2 505	873
	ASWB	1	E (Calorimetric)	R	*cis*	1 750	848
	DBC1	4	E (Spectroscopic)	G	*cis*	2 656	1 061
	DBC2	4	E (Spectroscopic)	G	*cis*	2 577	1 153
	DBC3	4	E (Spectroscopic)	G	*gauche*	2 057	965

[a] R = Rigid rotation; O = optimized in *ab initio* calculation; MM = optimized from molecular mechanics model;[26] G, based on geometry of glyoxal.[4] [b] The total energies of the *trans*-conformer in atomic units are E_T(PCL1) −154.4643, E_T(SB) −154.6931, E_T(SBS) −154.7461, E_T(PCL2) −154.7309, and E_T(RP) *ca.* −153.02. [c] These results are based on the four data points given by Skaarup *et al.*[10] (see Table 2) and may change somewhat when additional data points become available.

region. Furthermore, the formal double bond length in the calculations was much too short, and this may also have affected the shape of the curve.

(3) In going from the PCL1 curve to the PCL2 curve, which takes into account part of the electron correlation, there are only small changes in the vicinity of ϕ 0°. Although the lower two transitions, 0T—2T and 1T—3T, are not in quite such good agreement with experiment, the rest of the transitions are in better agreement. Furthermore, the spacings between transitions are increased with respect to those in PCL1, bringing them more in line with experiment.

TABLE 4

Decomposition of $V(\phi) = \Sigma Vn(1 - \cos n\phi)/2$ for various potential curves

Model	V_1	V_2	V_3	V_4	V_5	V_6
PCL1	274.5801	1 789.9451	908.9121	−301.8630		
SB	749.0125	1 413.5312	944.5491	−285.3401	112.8613	−38.4112
SBS	200.7970	1 383.3921	1 005.9551			
PCL2	−108.0830	1 892.1169	725.0310	−178.8090		
RP	418.6904	1 826.9175	498.0913	−189.5825	101.0873	−33.9290
C	600.0000	2 068.0000	273.0000	−49.0000		
ASWB	439.9741	1 309.2876	408.4067	151.6633	−0.1568	−43.5973
DBC1	941.0000	2 115.9000	119.9000	−10.9000		
DBC2	1 047.3000	1 997.1000	105.2000	51.7000		−17.1000
DBC3	469.1000	1 244.2000	909.0000	−177.1000		−19.8000

TABLE 5

Observed and calculated Raman overtone transitions (cm^{-1}) for the *trans*-conformer of buta-1,3-diene

Transition	Observed	PCL1 [8, a]		SB [7, b]	SBS [10, c]		PCL2 [8, a]		RP [6]	
0T—2T	323.0	334.7 [g]	334.5 [h]	346.5 [g]	392.9 [i]	383.4 [h]	337.1 [g]	337.0 [h]	326.8 [g]	326.6 [h]
1T—3T	317.6	330.8 [g]	330.6 [h]	340.2 [g]	382.2 [i]	373.2 [h]	331.3 [g]	331.1 [h]	320.7 [g]	320.5 [h]
2T—4T	312.5	326.5 [g]	326.2 [h]	333.3 [g]	371.0 [i]	362.7 [h]	325.2 [g]	324.8 [h]	314.3 [g]	313.9 [h]
3T—5T	306.2	321.8 [g]	321.4 [h]	325.9 [g]	359.4 [i]	351.7 [h]	318.7 [g]	318.4 [h]	307.4 [g]	307.1 [h]
4T—6T	300.6	316.5 [g]	316.2 [h]	318.1 [g]	347.3 [i]	340.2 [h]	311.9 [g]	311.6 [h]	300.0 [g]	299.8 [h]
5T—7T	293.7	311.0 [g]	310.7 [h]	309.7 [g]	334.5 [i]	328.1 [h]	304.6 [g]	304.2 [h]	292.2 [g]	291.9 [h]
6T—8T	286.4	304.8 [g]	304.4 [h]	300.6 [g]	320.7 [i]	315.3 [h]	296.7 [g]	296.4 [h]	284.0 [g]	283.6 [h]

Transition	ASWB [1, d]	C [3, e]		DBC1 [4]	DBC2 [4]	DBC3 [4]	Adjusted *ab initio* [f]	
							(*cis*)	(*gauche*)
0T—2T	322.2 [g]	324.4 [j]	327.5 [h]	323.4 [k]	322.8 [k]	322.3 [k]	323.1 [h]	322.4 [h]
1T—3T	315.5 [g]	318.4 [j]	321.6 [h]	317.8 [k]	317.8 [k]	318.0 [k]	317.7 [h]	317.9 [h]
2T—4T	308.0 [g]	312.3 [j]	315.5 [h]	312.1 [k]	312.4 [k]	312.9 [k]	312.2 [h]	312.9 [h]
3T—5T	299.4 [g]	306.0 [j]	309.2 [h]	306.1 [k]	306.5 [k]	307.1 [k]	306.4 [h]	307.2 [h]
4T—6T	289.7 [g]	299.5 [j]	302.7 [h]	299.9 [k]	300.3 [k]	300.6 [k]	300.5 [h]	301.0 [h]
5T—7T	278.9 [g]	292.8 [j]	295.9 [h]	293.6 [k]	293.6 [k]	293.3 [k]	294.3 [h]	294.0 [h]
6T—8T	266.7 [g]	285.1 [j]	288.8 [h]	287.0 [k]	286.5 [k]	284.9 [k]	287.7 [h]	286.1 [h]

[a] The Fourier analysis of the potential curve reported by these authors was used without change. [b] In making the Fourier analysis the energies of 0, 30, 60, 90, 120, 150, and 180° were employed and converted to cm^{-1}. [c] In making the Fourier analysis the energies given by these authors in kcal mol^{-1} were employed and converted to cm^{-1}. [d] In making the Fourier analysis the energies at 0, 30, 60, 90, 120, 150, and 180° were used, see equations in Figure 1 of ref. 1, and converted to cm^{-1}. [e] The Fourier analysis of the curve in ref. 3 was used without change. [f] *cis*-Case calculated from $2V(\phi) = 611.3181\ (1 - \cos\phi) + 2\,100.3933\ (1 - \cos 2\phi) + 255.1813\ (1 - \cos 3\phi) - 68.4741\ (1 - \cos 4\phi)$. The first three *cis*-well transitions ($\Delta\nu = 2$) from this potential curve are 271.2, 267.8, and 263.5 cm^{-1}. Gauche case calculated from $2V(\phi) = 739.9771\ (1 - \cos\phi) + 1\,133.3484\ (1 - \cos 2\phi) + 919.3832\ (1 - \cos 3\phi) - 126.0167\ (1 - \cos 4\phi) - 59.1966\ (1 - \cos 5\phi)$, giving transitions at 273.5, 264.4, and 255.7 cm^{-7} cm^{-1}. [g] Rigid rotation from experimental geometry [12] was used in computing $F(\phi)$. [h] Adjusted *ab initio* geometry was used (see Tables 1 and 2) in computing $F(\phi)$. [i] *Ab initio* geometry of Skaarup *et al.*[10] was used without change with F_0 3.2848, F_1 0.7242, F_2 0.3500, F_3 0.1358, and F_4 0.0452. [j] Consistent force field geometry of Allinger and Sprague [26] was used in computing $F(\phi)$. [k] The $F(\phi)$ employed is that of Durig *et al.*[4]

(4) Although the curve of Aston *et al.*[1] based on calorimetric data fits the first spectroscopic transition quite well, the spacings between the levels are too great, which indicates that the *trans*-well is too narrow. Moreover the peak position is predicted to be at *ca.* 70°, furthest from 90° of all the predicted values.

(5) A change from the rigid rotation model to the adjusted *ab initio* model with some flexibility has little effect on the energy levels *for a fixed potential curve* (see PCL1 and PCL2 in Table 5). However there is a more substantial effect in going from the modified *ab initio* model to the molecular mechanics model with its considerably greater flexibility (see C in Table 5). Furthermore, even though the transitions in SBS are based on a model with complete geometry optimization, a small improvement is nevertheless obtained with the model in which the C=C formal double bond is increased in length, more in keeping with the structural determination (see SBS in Table 5).

The spectroscopic results for the well associated with the less stable form are given in Table 6. The following points may be noted.

(1) With Carreira's *cis*-well, the transitions and spacings *do not* match the experimental values as closely as those for the *trans*-well. For example, the observed difference in the first *cis*-well transitions is 7.2 cm^{-1} whereas the predicted difference is only 4.5 cm^{-1}. To see if a modified geometry, with somewhat less flexibility, would result in better agreement, we have attempted to fit the observed transitions with the adjusted *ab initio* geometry (see Tables 1 and 2), using essentially Carreira's procedure. The *trans*-well transitions given in Table 5 are in the main slightly better than those obtained by Carreira. However, no better fit could be obtained for the *cis*-well, 271.2 cm^{-1} for the first transition and 3.4 cm^{-1} for the spacing between the first

and second transitions compared to the experimental values of 271.1 and 7.2 $\mathrm{cm^{-1}}$. The barrier height increased slightly from Carreira's value of 2 505 to 2 533 $\mathrm{cm^{-1}}$. Durig *et al.*[4] were able to get a better fit, particularly the spacing, but this was obtained only because of the relatively small F values they used near 180° (which are known to be in error [28]).

TABLE 6

Observed and calculated overtone transitions for *cis*- and *gauche*-conformers of buta-1,3-diene

A *cis*

Transition	Observed	ASWB	C	DBC1	DBC2	Adjusted *ab initio*
0C—2C	271.1 [a]	194.2	269.4	271.0	271.1	271.2
1C—3C	263.9 [a]	194.7	264.9	263.9	264.1	267.8
2C—4C	256.7 [a]	189.0	259.6	257.6	256.4	263.5

B *gauche*

Transition	Observed	PCL1	PCL2	SB	DCB3	RP	Adjusted *ab initio*
$0^+ \longrightarrow 2^+$	263.9 [b]	253.3	287.2	365.2	263.9	290.6	264.4
$0^- \longrightarrow 2^-$	271.1 [b]	319.9	347.6	370.5	272.2	372.5	273.5
$1^+ \longrightarrow 3^+$		266.0	373.2	309.2	216.9	385.6	214.4
$1^- \longrightarrow 3^-$	256.7 [b]	338.3	395.3	341.8	256.5	414.0	255.7

[a] Using the assignments of Carreira.[3] [b] Using the assignments of Durig *et al.*[4]

(2) Although there is good agreement (*i.e.* 1—7%) between the spectroscopic transitions predicted by the *ab initio* calculations and the experimental values localized in the *trans*-well, there appears to be little, if any, correlation between the transitions predicted from the *ab initio* calculations and the Carreira or Durig *et al.* assignment of frequencies to the second stable form. The difficulty is that *ab initio* calculations generally predict a rather low *gauche* — 180° energy difference which is inconsistent with a small spacing between levels

TABLE 7

Heat capacity $C_p°$ as a function of temperature calculated from the corresponding torsional potential curves

$C_p°$/cal $\mathrm{K^{-1}\ mol^{-1}}$ [a]

T/K	Experimental [22] [a]	PCL1 [b]	SB [b]	SBS [c]	PCL2 [b]	RP [b]	ASWB [b]	C [d]
220	14.73 ± 0.07	14.73	14.44	14.69	15.63	14.75	14.82	14.64
240	15.80 ± 0.08	15.81	15.44	15.80	16.66	15.81	15.91	15.66
260	16.91 ± 0.08	16.93	16.50	16.96	17.67	16.92	17.03	16.73
280	18.04 ± 0.09	18.07	17.59	18.15	18.68	18.05	18.19	17.82
300	19.19 ± 0.10	19.22	18.71	19.34	19.67	19.18	19.35	18.93
320	20.34 ± 0.10	20.36	19.84	20.53	20.65	20.31	20.51	20.04

	DBC1	DBC2	DBC3	Adjusted *ab initio* (*cis*)	Adjusted *ab initio* (*gauche*)
220	14.48	14.44	14.71	14.63	14.48
240	15.47	15.42	15.79	15.66	15.49
260	16.51	16.44	16.91	16.72	16.56
260	17.59	17.51	18.08	17.82	17.67
300	18.68	18.59	19.26	18.92	18.80
320	19.78	19.69	20.43	20.02	19.95

[a] 1 cal = 4.1833 J. [b] Rigid rotation with the experimental geometry of the *trans*-conformer [12] used to compute the torsional vibrational frequencies in calculating the partition function. [c] *Ab initio* geometry of Skaarup *et al.*[10] (see footnote *c*, Table 3) was used to compute the torsional vibrational frequencies in calculating the partition function. Similar results are obtained in the adjusted *ab initio* geometry described in Tables 1 and 2 is employed. [d] Molecular mechanics model for the rotation (see Tables 1 and 2) was used to compute the torsional vibrational frequencies in calculating the partition function.

(3) There is fair internal agreement among the calculations PCL1, PCL2, and RP with respect to the spacing between $0^+ \longrightarrow 2^+$ and $0^- \longrightarrow 2^-$ levels in a *gauche*-well. In view of the good agreement, to within a few $\mathrm{cm^{-1}}$, between the experimental spacings in the *trans*-well and those predicted using these basis sets, one is tempted to conclude that if the second stable form has a *gauche*-structure then the spacing between the two lowest levels is likely to be 60—80 $\mathrm{cm^{-1}}$. This is in sharp contrast to the assignments of Durig *et al.*[4] which would give a spacing of only 7 $\mathrm{cm^{-1}}$.

(4) The best agreement with the experimental data, assuming a *gauche*-well, is that obtained by Durig *et al.*[4] but incorrect $F(\phi)$ values were used.* We have carried out calculations similar to these assuming a *gauche*-well *with the same spectroscopic assignments*, but using the adjusted *ab initio* model for $F(\phi)$ and V_1—V_5 during the iteration. The transitions are listed in Tables 5 and 6. The barrier height was found to be 2 085 $\mathrm{cm^{-1}}$, the *trans* – *gauche* energy difference was 893 and the *gauche* — 180° energy difference 408 $\mathrm{cm^{-1}}$. The overall agreement with the observed spectrum is not quite as good as that found by Durig but is about the same as that found by Carreira with a *cis*-well. The spacing between the first two levels in the *gauche*-well is now too large, 9.1 compared with 7.2 $\mathrm{cm^{-1}}$.

B *Thermodynamic Calculations, $C_p°$ and $S°$.*—To calculate the contribution of the internal rotation to these functions the partition function was set up as the summation of the appropriate torsional energy level terms.[39] All sums were carefully checked for convergence. The remaining contributions to the thermodynamic functions were based on the RRHO approximation [39, 40] using the vibrational assignments of Shimanouchi.[23] While there is likely to be some interaction between the rotation and the torsion and between the torsion and other vibrations which

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* If $F(\phi)$ for the modified *ab initio* model is used with the Durig *et al.* potential curve, the spacing between the lowest transitions in the *gauche*-well increases from *ca.* 8 to nearly 20 $\mathrm{cm^{-1}}$. This suggests that an even larger *gauche* — 180° energy difference would be required for $F(\phi)$ in the *ab initio* or molecular mechanics model than that found in the Durig *et al.* calculation.

cannot easily be incorporated into the calculation, Pitzer[37] has noted that it is best to take all quantities appropriate to the equilibrium configuration and in a first approximation, to ignore changes in angle.*

In Table 7, C_p° is given as a function of temperature over the range 220—320 K, and compared with the experimental results.[22] Although all the values derived from the various potential curves are in fairly close agreement with experiment, there are some interesting differences.

(1) The variation of C_p° with temperature based on the *ab initio* calculation PCL2 gives the worst agreement, particularly at the lower temperatures. This can be traced back to the small energy difference between the *trans-* and *gauche*-forms, which results in too many energy levels below 1 000 cm^{-1}. These contribute significantly to C_p° in the temperature range covered, and hence lead to calculated values that are too large.

(2) The variation based on the *ab initio* calculation SB also gives relatively poor agreement. In this case, however, the calculated values are too small. This can be traced back to the relatively large energy differences between the *trans* − *gauche* form and *gauche* − 180° forms, larger than those obtained in any of the other *ab initio* calculations.

(3) The variation based on the *ab initio* calculations PLC1 and RP give the best agreement with experiment, usually differing by <0.03 cal K^{-1} mol^{-1}. In the PCL1 case this may be fortuitous, because the lower transitions localized in the *trans*-well differ by some 10—15 cm^{-1} from the observed values (see Table 5). As a consequence, there must be some compensation from the energy levels associated with the less stable form. On the other hand, the RP calculation does predict good spectroscopic data for the *trans*-well. In fact, the RP calculation is the only *ab initio* calculation which fits both the spectroscopic data and the C_p° data with good accuracy.

(4) The ASWB curve gives acceptable agreement as would be expected, since this curve was derived from the calorimetric data. However, this would also appear to be fortuitous since the transitions predicted for the *trans*-well are in poor agreement with the spectroscopic assignments of Carreira. It may be noted that our results differ slightly from the original calculations of Aston *et al.* because we have used a more up-to-date assignment of vibrational frequencies.[23]

(5) The C_p° values based on the curves C, DBC1, and DBC2 which predict the second stable form to have the *cis*-configuration lie considerably below the experimental results, and the discrepancy gets progressively bigger as the temperature increases.

(6) The adjusted *ab initio gauche*-model curve also gives rather poor agreement with experiment, which is contrary to that obtained from the DBC3 potential curve.

DISCUSSION

Assignment of the Low Frequency Raman Overtones.— The correct assignment of the transitions observed at 271.1, 263.9, and 256.7 cm^{-1} to either a *cis-*, or *gauche-*, or even the *trans*-well, would do much to further understanding of the torsional potential curve for buta-1,3-diene. In this section we shall examine in turn the consequences of making these various assignments.

(a) cis-*Well.* If the above transitions are assigned to a *cis*-well several points should be considered.

(1) The potential curve derived by Carreria does not fit the spacings between these levels particularly well, *i.e.*, a spacing of *ca.* 4.5 compared with the experimental value of *ca.* 7.2 cm^{-1}. Moreover, this spacing relates to the extremely flexible molecular mechanics model, and if the less flexible adjusted *ab initio* model is actually a better representation, the calculated spacing is reduced to only 3.4 cm^{-1}, less than half the experimental value.

(2) The heat capacity predicted from the Carreira, Durig *et al.*, and adjusted *ab initio cis*-wells are all less than the experimental values and the discrepancy gets worse the higher the temperature. This originates in the observed large spacing of 7.2 cm^{-1} which requires the *cis*-well to be rather narrow. In the calculation this is achieved by raising the barrier height above that determined by Aston *et al.* from calorimetric data by more than 750 cm^{-1}, and as a consequence lower values of C_p° result.

(3) The barrier heights of 7.2—7.7 cm^{-1} obtained by Carreira,[3] Durig *et al.*,[4] and the adjusted *ab initio* geometry model are greater than those predicted by most *ab initio* calculations. Many of these were obtained using rigid rotation models, and even lower values would be obtained with geometry optimization thus accentuating the difference. In addition both Dumbacher[9] and Pincelli *et al.*[8] found that if electron correlation is included in the calculation the barrier height is further reduced below the single determinant value. A further indication that the single determinant values for rotation about the central bond in buta-1,3-diene are likely to be somewhat higher and not lower than the experimental value is afforded by a comparison of results for ethane and for ethylene. For rotation about the single bond in ethane the calculated values usually agree with experiment to within 1 kcal mol^{-1}, whereas for rotation about the double bond in ethylene the calculated values are usually too high by *ca.* 60—70 kcal mol^{-1}.[6,41,42] In view of the ' partial double bond character ' of the central bond in buta-1,3-diene, it seems likely the *ab initio* barrier heights should be higher than the actual barrier height, not lower.

(4) *Ab initio* calculations almost invariably † suggest a *gauche*-well as do many recent semiempirical calculations such as MINDO/3,[44] NDDO,[43] and PCILO.[45]

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* This is true since it can be shown that ' changes in the mass or inertia factor for the various normal modes of vibration just cancel the changes in moment of inertia provided all motions are treated classically '.[37] Pitzer also notes that the method should yield results with errors not appreciably greater than the experimental errors for data available in 1945—1946. The experimental C_p° data on butadiene was obtained at this time.[22]

† There are two *ab initio* calculations that favour a *cis*-well. Radom and Pople[6] found using STO-3G that if the C–C=C angle was allowed to vary during the rotation (but *all* bond lengths and the remaining bond angles were held fixed) the well changed from *gauche* to *cis*. But studies by Devaquet *et al.*[46] in the 4-31G basis set, at completely optimized STO-3G geometries, found the *gauche*-form to be more stable. Dumbacher[9] also found a *cis*-well after CI, but he employed a geometry for buta-1,3-diene with a central C–C bond length of 1.483 Å, *ca.* 0.020 Å larger than the currently accepted value.[12] This would tend to lower the interaction between the terminal CH_2 groups near 180° and would favour a *cis*-configuration.

(5) N.m.r. data (although obtained in solutions) also suggest a *gauche*-well.[2]

In view of these considerations, there would appear to be no compelling reason for assigning the transitions at 271.1, 263.9, and 256.7 cm^{-1} to a *cis*-well.

(b) gauche-*Well*. If these transitions are assigned to a *gauche*-well the following points may be noted.

(1) The barrier height is lowered to 5.9—6.0 kcal mol^{-1}, lower than that predicted by the single determinant *ab initio* calculations that employ rigid rotation as would be expected.

(2) The relatively large spacing between the levels can be accounted for. We find 9.1 cm^{-1} using the *ab initio model* with V_1—V_5 in equation (1). If V_1—V_6 are employed this can be reduced to 8.9 cm^{-1}. Although these results are slightly high they differ from the experimental spacing by <2 cm^{-1} whereas Carreira's published curve based on a *cis*-well gives a difference of 2.7 cm^{-1}.

(3) The predicted variation of $C_p°$ with temperature is in relatively poor agreement with experiment for the adjusted *ab initio gauche*-model. This is caused by the relatively large *trans* — *gauche* energy difference of nearly 1 200 cm^{-1}. *Ab initio* calculations also suggest this should be lower (see Table 3) which would lead to better agreement.

(4) A relatively large *gauche* — 180° energy difference of over 400 cm^{-1} is predicted using the adjusted *ab initio* geometry model (see Table 7). Most *ab initio* calculations of the potential energy curve on the other hand, have suggested a somewhat smaller difference of 30—300 cm^{-1} which is also consistent with results using the PCILO method.[45] The SB calculation, however, found the energy difference to be over 600 cm^{-1}.

(5) The *gauche*-well obtained by Durig *et al.* as well as that based on the adjusted *ab initio* geometry requires a transition near 215 cm^{-1} (see Table 6). Although the region has been studied experimentally no such transition has been observed.[28]

(6) The potential curves derived from *ab initio* calculations strongly suggest a larger spacing (60—80 cm^{-1}) between the *gauche*-transitions, which is inconsistent with the 7.2 cm^{-1} spacing required by the Durig *et al.* assignment. It would seem somewhat unlikely that this large discrepancy could be caused by the omission of electron correlation because in going from the PCL1 with no correlation to the PCL2 calculation with some correlation the reduction is only from *ca.* 66 to 60 cm^{-1}.

Hence although in some respects of assignment of the transitions at 271.1, 263.9, and 256.7 cm^{-1} to a *gauche*- instead of a *cis*-well is more satisfactory, points (3)—(6) must be considered as evidence against this possibility.

(c) trans-*Well*. It could be that the peaks observed at 271.1, 263.9, and 256.7 cm^{-1} are due to higher level transitions in the *trans*-well. To explore this possibility, we consider again Carreira's potential curve. He already finds higher transitions at 270.8 and 262.7 cm^{-1} localized in the *trans*-well. These agree just as well with the observed transitions as his values of 269.2 and 264.7 cm^{-1} localized in the *cis*-well. If this were to be the case, however, it is then difficult to understand the discontinuity in the spectrum near 280 cm^{-1}.[3] The spectrum in this region is not devoid of structure and two small peaks are present on either side of 280 cm^{-1}. One of these peaks could clearly be a transition localized in the *trans*-well between the peaks assigned to this well at 271.1 and 286.4 cm^{-1}. In fact, the potential curve predicted by Carreira has a transition localized in the *trans*-well at 278.4 cm^{-1} with an intensity about one-third that of the transition at 286.4 cm^{-1}. With regard to the origin of the second peak, it may be noted that the RP (STO-3G) calculation, which predicts the low lying *trans*-well transition to within 3 cm^{-1}, predicts a *gauche*-well transition at 290.6 cm^{-1}. Since the lowest *trans*-well transitions are predicted to be a few cm^{-1} too high this could be the origin of the peak observed between 280 and 290 cm^{-1}. This is consistent with the PCL2 calculation which finds the ($0^+ \rightarrow 2^+$) transition at 287.2 cm^{-1}.*

To further investigate the likelihood that the peaks at 271.1, 263.9, and 256.7 cm^{-1} belong to the *trans*-well, we have carried out additional calculations fitting both the spectroscopic and thermodynamic data. All transitions from 323.0 to 263.9 cm^{-1} were assumed to be localized in the *trans*-well and the value of the $0^+ \rightarrow 2^+$ *gauche*-level was assumed to be *ca.* 283 cm^{-1}. (The transition observed at 256.7 cm^{-1} was dropped since it is the most uncertain value.) $C_p°$ was studied as a function of temperature over the range 220—320 K using the adjusted *ab initio* geometry to compute $F(\phi)$ and only V_1—V_4 in equation (1). With regard to the results listed in Table 8, we draw attention to the following points.

(1) Overall, the spectroscopic predictions are better than those of Carreira.[3]

(2) The $C_p°$ values never differ by more than 0.03 cal K^{-1} mol^{-1} from the experimental values, and are also in significantly better agreement than the values predicted from Carreira's curve (see Table 7).

(3) The barrier height of 6.6 kcal mol^{-1} is below the single determinant values of SB, PCL1, and Dumbacher,[9] and essentially the same as that obtained by Radom and Pople.[6] Although it is slightly above the SB value, this latter value is somewhat uncertain because only a few points on the potential curve were obtained and the maximum occurs at an angle below 90° where no points were obtained.

(4) A very low *gauche* — 180° energy difference of 30 cm^{-1} is predicted, which would lead to significant splitting of the degenerate levels found with deeper *gauche*-wells.

(5) A second *gauche*-well transition is predicted at 338.9 cm^{-1}. In the RP and PCL2 calculations this transition was found at 372.5 and 347.6 cm^{-1}, respectively. No attempt was made to adjust the value because it lies outside the range of the published spectrum

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* This interpretation of the data is *not* inconsistent with the PCL1 calculation, since (i) the *trans*-well transitions in this case are too high and (ii) the variation of $C_p°$ with temperature is very good which implies that the predicted *gauche*-well transition at 253 cm^{-1} is too low.

which extends only to 340 cm^{-1}. By using higher harmonics in equation (1), however, considerable adjustment could be made without any significant change in the $C_p{}^{\circ}$ values.

TABLE 8

Properties of the torsional potential curve based upon both spectroscopic and thermodynamic data

A Characteristic features

$$2V(\phi) = 347.2960(1 - \cos\phi) + 1\,790.0000(1 - \cos2\phi) + 612.7940(1 - \cos3\phi) - 179.7781(1 - \cos4\phi)$$

Barrier height 2 321 cm^{-1} (6.63 kcal mol^{-1}) at 82.8°

trans — *gauche* energy difference 930 cm^{-1} (2.66 kcal mol^{-1})

gauche — 180° energy difference 30 cm^{-1} (0.09 kcal mol^{-1})

B Predicted Raman frequencies (cm^{-1})

trans		Obs. — calc.[a]	*gauche*	
0—2	322.7	+0.3	0—2	282.3
1—3	317.7	−0.1	1—3	338.9
2—4	312.4	+0.1		
3—5	306.8	−0.6		
4—6	300.9	−0.3		
5—7	294.6	−0.9		
6—8	287.6	−1.2		
7—9	280.4	0.0		
8—10	272.5	−1.4		
9—11	263.8	+0.1		

C Predicted heat capacity (cal K^{-1} mol^{-1})

T/K	$C_p{}^{\circ}$	Obs. — calc.[b]
220	14.76	−0.03
240	15.83	−0.03
260	16.94	−0.03
280	18.07	−0.03
300	19.21	−0.03
320	20.34	0.00

[a] Experimental values taken from ref. 3. [b] Experimental values taken from ref. 22.

Taking into account all the various considerations in (a)—(c), it seems more probable that the transitions at 271.1 and 263.9 cm^{-1} are localized in the *trans*-well.

We have shown that it is possible to set up a potential curve for rotation about the central C–C bond in buta-1,3-diene which predicts both the torsional spectrum and the variation of $C_p{}^{\circ}$ with temperature quite accurately, and, in addition, is in substantial agreement with the results of *ab initio* calculations. This latter point we regard as important, since wherever an unambiguous comparison between theory and experiment can be made, for instance in the case of the torsional spectrum localized in the *trans*-well, there is good agreement between the two. Furthermore, the assignment of torsional frequencies as proposed either by Carreira or by Durig *et al.* does not result in such a good variation of $C_p{}^{\circ}$ with temperature, and is more at variance with the *ab initio* calculations.

But the potential curve which we have been led to propose, with only one of the observed transitions (*ca.* 283 cm^{-1}) assigned to a *gauche*-well, is nevertheless not unique, and its shape in this region is poorly determined. The curves proposed by Carreira and Durig *et al.* are, however, open to similar criticism, especially with regard to the peak height since none of the observed transitions involved levels above 1 500 cm^{-1} while the peak heights exceed 2 000 cm^{-1}.

In conclusion, it would appear to us that in order to make a more definitive choice for the structure of the second stable conformer of buta-1,3-diene further work is needed along the following lines.

(1) The Raman spectrum should be examined for additional torsional peaks from *ca.* 150 to 450 cm^{-1}.

(2) A similar Raman spectrum should be obtained for deuteriated butadienes. Some data of this kind are already available,[24] but only the lower transitions located in the *trans*-well were observed. We have calculated the spectrum for [1,1,4,4-$^2H_4$]buta-1,3-diene using the potential curve of Table 8. The three lowest transitions calculated for the *trans*-well agree with experiment to within 0.3 cm^{-1}. The lowest transition localized in the *gauche*-well is predicted to be at 253 cm^{-1}, a frequency which is lower than the first eleven localized in the *trans*-well.

(3) Additional *ab initio* calculations with complete geometry optimization are called for. The problem with previous calculations, *e.g.* at a single ζ level such as STO-3G, is that the central single bond in *trans*-buta-1,3-diene is found to be *ca.* 0.025 Å too long, and the double bond(s) *ca.* 0.030 Å too short.[29-31] Hence, if geometry optimization were to be carried out at this level of calculation, the results would necessarily be suspect because the molecule would be highly distorted. This problem, however, now seems near resolution. The basis set used in the SBS calculations is already adequate with regard to predicting the length of the single bond, actually giving the experimental value of 1.463 Å and, although the length of the double bond was still found to be too short by *ca.* 0.020 Å, Jaszunski *et al.*[47] have recently reported calculations on ethylene using a double ζ basis set with geometry optimization that gives a double bond length of 1.335 Å in excellent agreement with experiment. There is thus good reason to believe that calculations at an appropriate double ζ level with full geometry optimization would do much to clarify the nature of the torsional potential curve for buta-1,3-diene, and with it the structure of the less stable form.

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