

The Geometries of the *s*-Cis Conformers of Some Acyclic 1,3-Dienes: Planar or Twisted?

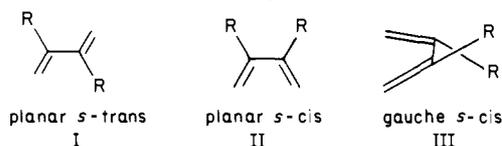
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Abstract: We have established a method to determine the geometry of the minor forms of acyclic 1,3-dienes. A high vacuum cryogenic trapping technique was used to obtain spectral data of these metastable conformers from mixtures equilibrated at 1100 K. This has enabled us to characterize the minor form of 2,3-dimethyl-1,3-butadiene (DMB) by IR and UV spectroscopy. Barriers to rotation of the metastable forms of isoprene and DMB to their stable *s*-trans forms have also been obtained. The UV spectra of acyclic 1,3-dienes are found to be determinant of structure and, on this basis, we assign a planar *s*-cis molecular framework to 1,3-butadiene and isoprene, and a *gauche* *s*-cis geometry to DMB.

Acyclic 1,3-dienes represent the simplest conjugated system, and as such they have generated considerable interest over the years. It is generally recognized that most acyclic 1,3-dienes exist as a mixture of two conformers.¹ In most cases the more stable conformation is planar and *s*-trans about the central bond (I),² while the minor form presumably has an *s*-cis configuration. Much 1,3-diene chemistry proceeds through this minor conformer, but amazingly its exact structure is still a matter of debate and no method has been firmly established to determine the geometries of the less stable isomers of acyclic 1,3-dienes.³

The question of the structure of the minor form of 1,3-dienes revolves about the magnitude of the dihedral angle of the central bond. Two possible conformations exist for the *s*-cis form: planar (II) with a dihedral angle of 0°, and *gauche* (III) with a dihedral angle between 0° and 90°. The planar configuration maintains



maximum conjugation across the diene unit, while the *gauche* form relieves nonbonded strain between the two terminal methylene groups and between substituents at the 2 and 3 positions. A balancing of these two factors determines the geometry that is adopted by the less stable conformer of 1,3-butadiene and its simple derivatives.

A variety of spectroscopic techniques have been used in attempts to determine the structure of the minor conformer. These investigations have centered upon the parent compound, 1,3-butadiene, but have suffered from ambiguities inherent in the various techniques. The observed temperature dependence of NMR parameters led to the opinion that the *s*-cis conformer had a *gauche* geometry,⁴ but large correlated errors mitigated this conclusion.⁵ Analysis of both infrared⁶ and Raman^{7,8} vibrational spectra gave results too ambiguous to unequivocally delineate the structure of the minor isomer of 1,3-butadiene.

It was predicted some time ago,⁹ on the basis of calculations and model systems, that the ultraviolet maxima of planar *s*-cis-1,3-dienes should be red-shifted from the maxima of the corresponding planar *s*-trans form. The maxima of the corresponding *gauche* *s*-cis forms were predicted to be blue-shifted from those of the *s*-trans forms, with the amount of the shift increasing with the angle twist around the central bond. These predictions cannot be used to test for the metastable conformers at room temperature because the mole fractions are too small for deconvolution of the UV spectrum.¹⁰ However, by employing a technique of equilibration at high temperature followed by cryogenic trapping,¹¹ the mole fractions can be increased and the spectra easily deconvoluted.

When this technique was applied to 1,3-butadiene it was shown that the minor form had a UV maximum red-shifted from the major *s*-trans rotamer.⁵ This was taken as evidence that the higher energy conformer of 1,3-butadiene had a substantial conjugation and thus a small dihedral angle (less than 15°). The absence of corroborating evidence has prevented the general acceptance of this conclusion.^{6,12}

Molecular force-field calculations have found a planar geometry for *s*-cis-1,3-butadiene.¹³ However, a number of recent ab initio calculations find that the minor form of acyclic 1,3-dienes has a substantial dihedral angle, even though the energy of the planar *s*-cis form is only slightly higher.^{3b,12,14} The most recent calculation, performed with a very high-level basis set, finds that a *gauche* form with a dihedral angle of about 35° is preferred by 0.81 kcal/mol over the planar form.¹² These authors have suggested that the distinction between the planar and *gauche* geometries may be "difficult to make on an experimental basis".¹²

To address this problem we felt it was necessary to establish a spectroscopic method which could unambiguously determine the conformational preference of the minor forms of acyclic 1,3-dienes. We sought, therefore, to test the proposal that the geometries of these minor forms could be determined from their UV spectra, and we chose 2,3-dimethyl-1,3-butadiene (DMB) as our probe of this hypothesis.

DMB has significantly more nonbonded strain than 1,3-butadiene itself. Thus it is much more likely that DMB has a *gauche* geometry for the *s*-cis isomer. If the UV spectrum of the minor

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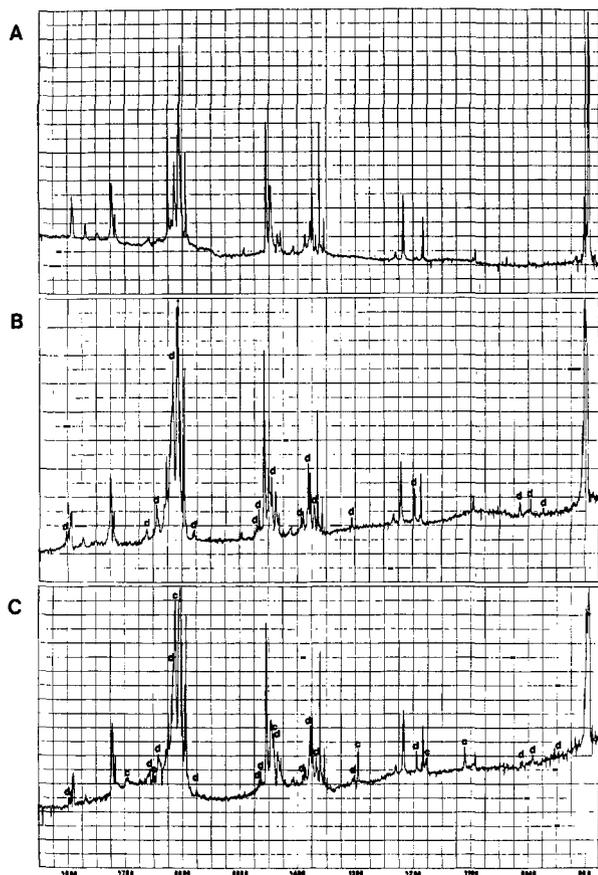


Figure 1. FTIR spectra (1850 to 875 cm^{-1}) of matrix-isolated DMB (1:1000 in argon) at 19.3 K. For a listing of bands see Table I. (A) DMB is deposited from room temperature. (B) DMB is deposited from 1100 K; the bands labelled d are due to *s-cis*-DMB. (C) Spectrum of sample B after 90-min irradiation with a 1000-W Hg-Xe arc lamp; the bands labeled c are due to the photoproduct, 1,2-dimethylcyclobutene.

form of DMB is red-shifted from that of the *s-trans* form by an amount similar to that found for the parent compound 1,3-butadiene,⁵ then either all acyclic 1,3-dienes have the same minor conformer geometry, presumably *gauche*, or their UV spectra are insensitive to geometry changes. It will be shown, however, that the UV spectrum of DMB varies by a substantial blue shift from that seen for 1,3-butadiene and that the UV spectra of the minor forms of acyclic 1,3-dienes are in fact determinate of their structures.

Experimental Section

The 2,3-dimethyl-1,3-butadiene and isoprene (Gold Label) were purchased from Aldrich and used without further purification. A Digilab FTS-15B FT-IR, a Perkin-Elmer 552A UV/VIS spectrophotometer, and a WM-250 Bruker NMR were used to obtain the spectral data. A 1000-W Xe(Hg) arc lamp was used as the light source for all photolysis experiments. Low-temperature IR and UV spectra were taken by using an Air Products CS-202 Displex equipped with an APD-E temperature controller. The Displex was fitted with external KBr windows and an internal CsI plate for the infrared experiments. External supracil quartz windows and an internal sapphire plate were mounted for the UV experiments.

Samples were deposited neat or diluted 1000:1 in argon by passing the vapor through a quartz tube oven (3-mm i.d.) and letting the gas impinge upon the cooled internal window, approximately 3 cm away from the end of the oven. The heating of the oven was achieved by wrapping the last 4 cm of the quartz tube tightly with a tantalum resistance wire. The temperature was measured with a chromel-alumel thermocouple placed in the flowing gas. For the IR matrix isolated experiments, deposition time was 4–6 h at a deposition rate of about 0.0026 mmol of DMB/h. The IR spectra were all taken at 0.75- cm^{-1} resolution. For the UV matrix isolated experiments the time of deposition was 0.5 h, with a deposition rate of 0.0022 mmol of DMB/h. The neat samples were deposited as a gas with a back pressure of 200 μm directly from a liquid source. The amounts deposited were about 0.12 mmol.

Table I. Infrared Spectra of the Two Forms of 2,3-Dimethyl-1,3-butadiene

planar <i>s-trans</i> ^a		<i>gauche s-cis</i> ^a	
neat	matrix isolated	neat	matrix isolated
3095 (0.18)	3114 (0.07)	3080 (0.09)	3088 (0.14)
3020 (0.05)	3107 (0.02)	2945 (0.33)	2950 (0.23)
3005 (0.04)	3101 (0.09)	2920 (0.11)	2929 (0.10)
2990 (0.16)	3097 (0.22)	1637 (0.09)	2927 (0.06)
2975 (0.37)	3012 (0.03)	1615 (0.06)	2922 (0.06)
2947 (0.32)	3008 (0.06)	1432 (0.29)	2895 (0.04)
2930 (0.16)	2999 (0.07)	1388 (0.14)	1798 (0.15)
2910 (0.12)	2994 (0.14)	1385 (0.13)	1793 (0.09)
2860 (0.07)	2986 (0.19)	1365 (0.04)	1641 (0.18)
1601 (0.85)	2980 (0.18)	1298 (0.03)	1628 (0.15)
1590 (0.07)	2962 (0.20)	1195 (0.06)	1615 (0.13)
1452 (0.34)	2958 (0.10)	1015 (0.03)	1575 (0.05)
1445 (0.32)	2953 (0.20)	966 (0.03)	1467 (0.08)
1440 (0.26)	2939 (0.17)	898 (1.00)	1463 (0.20)
1377 (0.21)	2934 (0.14)		1443 (0.20)
1372 (0.34)	2913 (0.08)		1441 (0.34)
1184 (0.11)	2873 (0.03)		1391 (0.10)
1036 (0.04)	2858 (0.03)		1380 (0.08)
995 (0.05)	1791 (0.21)		1366 (0.14)
920 (0.07)	1789 (0.18)		1302 (0.06)
890 (1.00)	1624 (0.06) ^b		1194 (0.24)
	1611 (0.07) ^b		1012 (0.08)
	1606 (0.07) ^b		992 (0.13)
	1603 (0.39)		970 (0.03)
	1599 (0.58)		913 (0.05)
	1593 (0.05)		906 (0.06)
	1572 (0.04)		897 (1.00)
	1492 (0.03)		894 (1.00)
	1453 (0.45)		761 (0.08)
	1446 (0.25)		664 (0.05)
	1434 (0.07)		662 (0.05)
	1408 (0.02)		558 (0.05)
	1386 (0.08)		533 (0.04)
	1378 (0.14)		
	1374 (0.26)		
	1184 (0.17)		
	1093 (0.03)		
	1036 (0.03)		
	997 (0.02)		
	915 (0.02)		
	901 (0.10)		
	893 (1.00)		
	885 (0.04)		
	657 (0.05)		
	529 (0.04)		
	521 (0.03)		
	468 (0.07)		

^a Absorption frequencies in cm^{-1} ; relative intensities in parentheses.
^b H_2O .

Results

Gaseous DMB was passed through the quartz tube at 1100 K and allowed to impinge on a CsI plate at 24.7 K. The IR spectrum of this neat sample showed bands which were not present in the IR of a neat sample deposited from room temperature (Table I). When the CsI plate was warmed to 60 K, these extra bands rapidly disappeared; the bands corresponding to the *s-trans* form increased and the remaining spectrum was identical with that of the room temperature sample. No decomposition was observed.

A DMB/argon mixture (1/1000) was then deposited from 1100 K onto a CsI window cooled to 19.3 K (Figure 1). Bands were again observed which were either not present or present with only weak intensity in the IR obtained from deposition of a room temperature sample (Table I). Because matrix isolation affords much higher resolution, more additional bands of the metastable species were observed, but overall these corresponded closely to the extra bands found from the deposition of a neat sample from 1100 K. Annealing the matrix-isolated sample to the highest possible presublimation temperature of 39 K did not result in the disappearance of the additional bands. That the additional bands seen in the neat deposition experiments were not due to crystal effects was shown by the fact that they were present in the matrix

isolation experiments. Furthermore, bands seen in the matrix isolation experiments cannot be due to site splitting since these bands would have disappeared upon annealing. These results, combined with the warming experiments performed on the neat depositions, establish the metastable species as the minor conformer of DMB.

From a neat sample deposited from 1100 K, rates of decay of the minor form were measured at 45.0, 45.5, and 46.0 K by warming of the CsI window and following the decay with time of the 1015 and the 1195 cm^{-1} bands. By use of the absolute rate equation, the free energy of activation for the conversion of the *s*-cis to *s*-trans isomer was calculated to be 3.4 ± 0.1 kcal/mol. Rotation around the central bond of DMB also occurred in a Xe matrix at about the same temperature as in the neat sample, but a rate study could not be performed because a clear matrix with sufficient signal to noise could not be obtained.

A sample of isoprene was similarly deposited from 1100 K. Rates of decay of the minor form were measured by monitoring the previously identified bands¹⁵ at 1077 and 1244 cm^{-1} as a function of time at 52.0, 53.0, and 54.0 K. Analysis of these decay rates gave a ΔG^\ddagger of 3.9 ± 0.1 kcal/mol for the conversion of the minor to major conformer.¹⁶

Another useful aspect of the high-temperature trapping technique used here is shown by the easy identification of previously unrecognized¹⁷ infrared bands belonging to the minor form in a matrix-isolated sample of DMB deposited from room temperature. From the high-temperature deposition of DMB, bands at 897 and 1194 cm^{-1} had been identified as minor form bands. Our UV results show that from 1100 K a ratio of approximately 60:40 *s*-trans to *s*-cis isomer is trapped. This ratio is mirrored by the intensities of the similar 893- and 897- cm^{-1} bands and the 1184- and 1194- cm^{-1} bands of the *s*-trans and *s*-cis isomers, respectively, as can be seen in Figure 1B. This implies nearly equal extinction coefficients for these pairs of bands. From the heights of the pairs of peaks at room temperature, K_{eq} was estimated to be about 18.5, which yields a ΔG°_{293} of 1.7 ± 0.2 kcal/mol. While ΔS° has not been measured, an entropy of mixing of the two gauche forms would give a value of $R \ln 2$. The shallow potential surface of a planar *s*-cis form would also be expected to give an entropy difference of roughly this same magnitude.¹⁸ Thus, assuming a ΔS° value of $R \ln 2$, a ΔH°_{293} can be calculated to be 2.1 ± 0.2 kcal/mol.

A DMB/argon mixture (1:1000) was deposited from both room temperature and 1100 K onto a sapphire window precooled to 19.3 K. As seen in Figure 2, the UV spectrum of the sample deposited from high temperature shows an absorption blue-shifted from the maximum of the sample deposited from room temperature. By analogy to the infrared experiments this band must be due to the *s*-cis conformer of DMB.

A good estimate of the UV absorption spectrum of the high-energy conformer can be obtained by subtraction of the UV spectrum of a sample deposited from high temperature from the spectrum of a room-temperature deposition of the same amount of material. Since the mole fraction, a , of the *s*-cis form present in the high-temperature deposition is not known, various values of a were assumed. It was found that for the UV spectrum of the minor form to be greater than zero at all wavelengths and for the spectrum to show the expected smooth band shape, a had to be greater than 0.35. When a is greater than or equal to 0.35, the absorption spectrum becomes fairly insensitive to the chosen value of a . In particular, λ_{max} for the UV spectrum stays constant at 217 nm while the overall band shape shows little variation. The main effect of altering the value of a is that the ratio of the extinction coefficients of the two conformers changes. The room-temperature deposition contains a small amount of the minor isomer, less than 5%. However, the final results do not change noticeably when this is taken into account. Eventually, we suc-

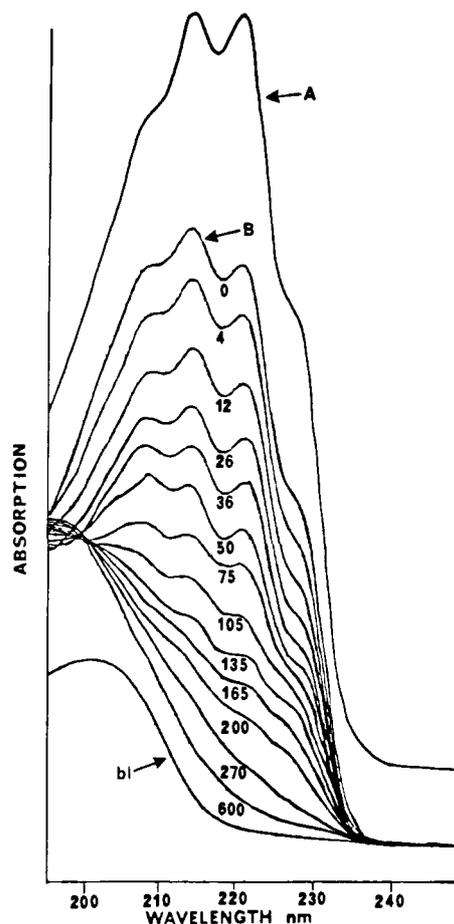


Figure 2. (A) UV spectrum of matrix-isolated DMB (1:1000 in argon) at 19.5 K, deposited from room temperature. (B) Series of UV spectra of a sample of matrix-isolated DMB (1:1000 in argon) at 19.5 K, deposited from 1100 K, undergoing a photochemical conversion to 1,2-dimethylcyclobutene. Irradiation time in minutes is indicated under each trace. Spectra are not corrected for baseline absorption (bl).

ceeded at evaluating a as 0.42 by a kinetic method which will now be described.

Photolysis of a matrix-isolated sample of DMB deposited from 1100 K gave only 1,2-dimethylcyclobutene¹⁹ as a product, as shown by FTIR and FTNMR. Infrared spectra taken during the 1–2-day photolysis period showed a disappearance of the minor form, a slower disappearance of the major form, and an increase in the product equal to the disappearance of both isomers (Figure 1). Unlike 1,3-butadiene⁵ and isoprene,¹⁵ no rapid photoequilibration of rotamers occurred. Photolysis of a matrix-isolated sample of DMB deposited from room temperature again gave only 1,2-dimethylcyclobutene as a product. Infrared spectra taken during the photolysis period showed a slow disappearance of the major form and a slow rise in the appearance of the photoproduct. The low-intensity minor form IR peaks observable in the original spectrum quickly disappear upon photolysis.

The rapid photoequilibrium in 1,3-butadiene resulted in changes in the UV spectrum which could be used to obtain the UV spectrum of the minor form.⁵ The lack of rapid photoequilibration of DMB isomers is astonishing when one considers that more than 100 kcal/mol of energy is being deposited into the molecule yet apparently only rarely does a small fraction of this energy (3.4 kcal/mol) become available to rotate the central bond of DMB. However, the lack of photoequilibration in DMB demanded that a new method be found to be obtain the UV spectrum of the minor isomer.

When the photolysis of a matrix-isolated sample of DMB deposited from 1100 K is monitored by UV spectroscopy, a very nice

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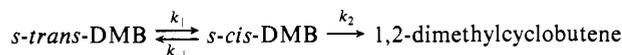
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series of spectra results (Figure 2). As can be seen from Figure 2, an isobestic point appears after 75 min of photolysis and remains for the duration of the experiment. A slower decay of the remaining spectrum occurs, and after 10 h of photolysis only the weak UV absorption of the cyclobutene product is seen. These results mirror those of the infrared experiments. There is a fairly rapid photochemical closure of the *s-cis* form initially present. When essentially all the initial *s-cis* form is depleted, an isobestic point is established where the extinction coefficients of the *s-trans* form and the photoproduct, 1,2-dimethylcyclobutene, are identical. The remaining *s-trans* form is slowly converted to the cyclobutene via a very small steady-state concentration of *s-cis* form produced from the slow photoequilibrium. The following indicates this process.



Because the matrices are very thin films, the photochemical rate constants can be approximated by linear rate constants. The changes in the areas of the UV spectra with photolysis time were fit to the general solutions for this kinetic problem²⁰ by use of a nonlinear least-squares calculation based on the general statistical method of Wentworth and Deming.^{21,22} The program was modified to run on an IBM PC, and would fit as many as five parameters. It would take up to ten variables and any number of constants in fitting these parameters. The molar absorptivity of the minor form, k_1 , k_{-1} , and k_2 were the parameters to which the data were fit. The molar absorptivities of *s-trans*-DMB and 1,2-dimethylcyclobutene were obtained from UV spectra of samples deposited from room temperature and were entered as constants into the program. The equations were then fit to various values of starting ratio of *s-trans* to *s-cis* form. The best fit to the data was for an initial *s-trans* to *s-cis* ratio of 58:42 with values for the rate constants of $k_1 = 1.36 \pm 0.04 \text{ E-4}$, $k_{-1} = 2.4 \pm 2.0 \text{ E-5}$, and $k_2 = 1.30 \pm 0.09 \text{ E-3}$. Since each UV trace after the isobestic point was due to only the cyclobutene product and *s-trans*-DMB, the appropriate amount of product could be subtracted out, leaving a spectrum of the *s-trans*-DMB present at that time. By use of the rate constants, this spectrum could then be extrapolated to give a UV spectrum corresponding to the amount of *s-trans* form present before photolysis. Subtraction of this spectrum from the original UV yielded the UV of the minor form. As can be seen from Figure 3, the major form has a maximum at 222 nm, whereas λ_{max} of the minor form is located at 217 nm, in agreement with our earlier estimate. Comparison of the *s-trans* UV spectrum obtained in this manner to a UV spectrum of a room-temperature deposition of DMB showed that the room-temperature sample contained about 4% of the minor form. This yields a ΔG°_{293} of about 1.85 kcal/mol and assuming a ΔS° of $R \ln 2$, a ΔH°_{293} of 2.25 kcal/mol.

Discussion

DMB, like isoprene and 1,3-butadiene, has two minima on the potential surface generated by rotation around the central carbon-carbon bond. For all three substances the global minimum occurs at a dihedral angle of 180°, which corresponds to the planar *s-trans* configuration. In the work presented here, we have gained spectroscopic, thermodynamic, and photodynamic information on the minor form of DMB and have firmly established a method for determining the geometry of the *s-cis* form of acyclic 1,3-dienes.

The technique of cryogenically trapping a high-temperature equilibrium mixture has enabled us to obtain the infrared spectrum of the minor form of DMB. A large number of *s-cis* bands were identified (Table I), but no attempt was made to use these frequencies to determine the *s-cis* geometry because previous attempts to determine the minor form geometry of 1,3-butadiene in this

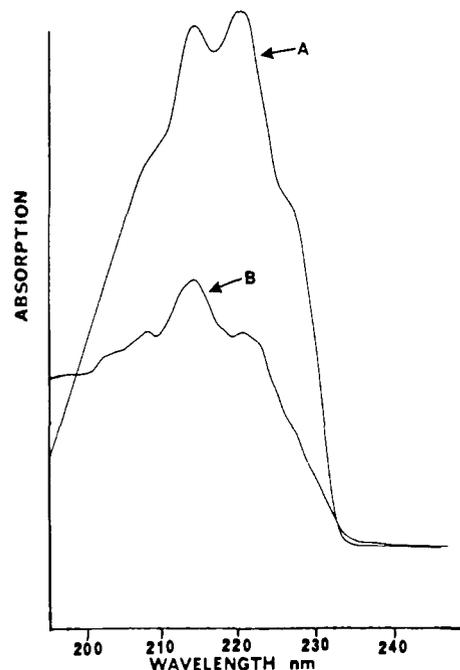


Figure 3. (A) UV spectrum of *s-trans*-DMB (contains about 4% *s-cis*). (B) UV spectrum of gauche *s-cis*-DMB. Both spectra corrected for baseline absorption.

manner led to equivocal results.⁶

The power of the trapping technique used here is revealed by the fact that we can now easily assign low-intensity peaks present in room-temperature depositions to the minor form. We can use these bands to gain some idea of the room-temperature ratio between the two forms of DMB. The 893- and 897-cm⁻¹ asymmetric CH₂ wagging modes and the 1184- and 1194-cm⁻¹ asymmetric CH₃ rocking modes of *s-trans* and *s-cis* forms, respectively, were shown to have very similar extinction coefficients. Thus the ratio of these pairs of bands reflects the room-temperature conformer ratio and gives a ΔG°_{293} of 1.7 kcal/mol. Whether the *s-cis* form is gauche or has a shallow minimum at the planar geometry it should have a substantial entropy. If we assume a ΔS° value of about $R \ln 2$, we obtain a ΔH°_{293} value of 2.1 kcal/mol. This agrees very well with the results of the UV experiments, which give a ΔH°_{293} of 2.25 kcal/mol. Since the errors in these values depend upon the trapping efficiency, we estimate an uncertainty of 30% in these thermodynamic parameters.

The photodynamics of the DMB system is strikingly brought out by the UV spectra shown in Figure 2. There is a fast closure of the initial *s-cis*-DMB present to 1,2-dimethylcyclobutene followed by a much slower photoequilibration of *s-trans* to *s-cis* form, which quickly closes. Interestingly, this may be the first spectroscopic evidence for the long established presumption that closure of an acyclic 1,3-diene to a cyclobutene proceeds through an *s-cis* geometry. The very slow photoequilibration of DMB isomers as compared to the isomers of 1,3-butadiene and isoprene is puzzling. The lack of rotation about the central bond, when more than 100 kcal/mol of energy is put into the molecule, may imply a nonrandom energy distribution during the radiationless decay process. More aspects of this phase of DMB photochemistry are being investigated.

An analysis of the UV data presented in Figure 2 gives a λ_{max} for *s-cis*-DMB of 217 nm and a ratio of extinction coefficients of *s-cis* to *s-trans* form of 0.48. In a theoretical study of UV spectra of polyenes, Allinger and Miller obtained a value of 0.465 for the ratio of the extinction coefficients for planar *s-trans* and *s-cis* 1,3-butadiene at their respective λ_{max} .⁹ This is in good agreement with the experimental value of 0.45.⁵ These workers also determined that this ratio will stay constant up to a twist angle of 30° from the planar *s-cis* form and then decrease slowly with increasing dihedral angle to a value of 0.4 for a twist angle of 60°. A recent paper by Chenera and Reusch cited low molar absorp-

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Table II. UV Absorption Maxima for 1,3-Dienes with Their Respective Barriers

substituents	<i>s</i> -trans, nm	<i>s</i> -cis, nm	ΔG^\ddagger , kcal
2-H, 3-H	212	226	3.9
2-CH ₃ , 3-H	217	231	3.9
2-CH ₃ , 3-CH ₃	222	217	3.4
2- <i>t</i> -Bu, 3- <i>t</i> -Bu	186 ^a		

^a Dihedral angle near 90°.

tivity for two similar polyenes as evidence for *s*-cis geometries.²³ Our extinction coefficient ratio of 0.48 for DMB and the value of 0.45 for 1,3-butadiene suggest that indeed low molar absorptivities of 1,3-dienes indicate an *s*-cis geometry, but also agree with the calculations of Allinger and Miller which show that the extinction coefficient ratio is relatively insensitive to *s*-cis geometry differences.

In contrast, to the extinction coefficients, comparison of the UV maxima of DMB, 1,3-butadiene, and isoprene leads to a firm conclusion concerning the geometries of the minor forms of these compounds. As seen in Table II, there is a smooth 5-nm progression of λ_{\max} for the *s*-trans forms of this series as predicted by the Woodward rules.²⁴ Both this fact and other spectroscopic evidence^{2b} suggest that the major forms of each of these compounds have a constant molecular framework, the planar *s*-trans geometry. In the *s*-cis forms of this series there is a 5-nm red shift between *s*-cis-1,3-butadiene and *s*-cis-isoprene, again indicating a constant molecular framework. If DMB was characterized by this same molecular framework, it would have a λ_{\max} at 236 nm. However, *s*-cis-DMB shows a considerable *blue shift* of about 20 nm from this predicted value. This large discrepancy indicates that the geometric structure of the minor conformer of DMB *must be substantially different* from the similar geometry which is possessed by the *s*-cis forms of 1,3-butadiene and isoprene. If it is assumed that this geometry difference is due to different 2,3 torsional angles, then two possibilities arise:

Case 1. *s*-cis-1,3-Butadiene and -isoprene are planar or nearly so, and *s*-cis-DMB is twisted by about 30–50°.

Case 2. *s*-cis-1,3-Butadiene and -isoprene are twisted approximately 30–50°, and *s*-cis-DMB is twisted by about 60–80°.

We believe that the former possibility is indeed the case.

This conclusion is supported by two pieces of information. The first is the value of the UV maximum of *s*-cis-DMB. As seen in Table II, 2,3-di-*tert*-butyl-1,3-butadiene has a λ_{\max} of 186 nm which is characteristic of substituted ethylenes.²⁵ This molecule exists as only one conformer, presumably the 90° twisted form. If *s*-cis-DMB were highly twisted (case 2), then it too should show a λ_{\max} near 186 nm. On the other hand, if case 1 holds, then a λ_{\max} for the twisted *s*-cis-DMB can be predicted using a $\cos^2 \theta$ dependence for the overlap of the two ethylene units.²⁴ With limits of 186 nm for a completely unconjugated DMB (90° twist), and 236 nm for a planar *s*-cis-DMB as per the Woodward rules (0° twist), a twist of 38° around the central bond would put the λ_{\max} at 217 nm. This is the observed value and agrees well with the angle dependence of λ_{\max} predicted by Allinger and Miller.⁹

The second piece of information supporting our belief that case 1 holds is the small difference between the *s*-cis to *s*-trans barriers of 1,3-butadiene and isoprene and that of DMB. As seen from Table II, the *s*-cis form of DMB has a barrier of conversion to *s*-trans-DMB greater than 85% of the barrier found in 1,3-bu-

tadiene and isoprene. This small difference is expected only for case 1 since much more delocalization is lost during the final 30° of a 90° rotation than is lost during the initial 30° of rotation from a planar geometry.²⁶ Thus, going from a planar *s*-cis structure to a structure twisted by 30–40° (case 1) should result in only a small loss in delocalization and a small difference in barrier heights, while going from a slightly twisted *s*-cis geometry to a severely twisted *s*-cis form (case 2) would sharply diminish the amount of delocalization and result in a substantial change in barrier heights. The portion of the torsional barrier not due to delocalization should show little difference between case 1 and case 2. Again we are led to believe that case 1 applies and that *s*-cis-1,3-butadiene and -isoprene are planar and *s*-cis-DMB is slightly twisted.

While our conclusion does not agree with a number of recent *ab initio* calculations on this system,^{3b,12,14} it should be pointed out that all of these investigations show differences in energy between the *gauche* and planar forms of *s*-cis-1,3-butadiene of less than 1 kcal/mol. A closer examination of one of these *ab initio* calculations¹⁴ shows nearly identical potential energy surfaces for the rotation about the central bond for 1,3-butadiene and isoprene, while the energy surface for DMB is substantially different. It was predicted by these authors that the *s*-cis forms for all three-compounds would have nearly identical twist angles of 44°. This result is clearly contrary to the UV spectra we have obtained. However, the well about the *gauche s*-cis form of DMB was found to be more than twice as deep with a calculated *gauche*:planar *s*-cis energy difference of 2.3 kcal/mol.^{14b} Furthermore, the *s*-cis to *s*-trans barriers found by this and other calculations are consistently smaller than our experimentally measured values for all three compounds. This suggests that these calculations underestimate the amount of electron delocalization present in the 1,3-diene system, which would naturally lead to a preference of *gauche* over planar *s*-cis geometries.

Conclusion

The technique of high-temperature equilibrium cryogenic trapping allowed us to obtain thermodynamic and kinetic parameters of DMB. From a sample of DMB trapped from room temperature, a ΔG^\ddagger_{293} could be calculated to be about 1.8 kcal/mol. Through a kinetic study, DMB was found to have an activation barrier for the *s*-cis to *s*-trans conversion of 3.4 kcal/mol while isoprene and 1,3-butadiene both have a barrier of 3.9 kcal/mol. We have also established that the UV spectra of the *s*-cis forms of 1,3-dienes are indicative of their geometries, and while the potential surface about all of these minor isomers is undoubtedly quite shallow, their UV spectra show that their respective zero-point torsional levels are bound at different points of their ground-state potential surfaces. Thus *s*-cis-DMB can be considered to have *gauche* geometry while *s*-cis-1,3-butadiene and -isoprene have planar geometries.

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Registry No. DMB, 513-81-5; 1,3-butadiene, 106-99-0; isoprene, 78-79-5.

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