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s-Cis vs. Gauche 1,3-Butadiene: Evidence for Planarity from Polarized Matrix-Isolation IR Spectroscopy

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Abstract: Irradiation of neat or matrix-isolated samples of the two conformers of 1,3-butadiene, obtained by deposition through a ~1200 K oven onto a 10 K CsI substrate, with linearly polarized 248-nm light causes photoselection and produces partially oriented solid solutions of both conformers. The dichroic ratios of the IR bands were used to determine IR transition-moment directions. The IR transition-moment directions of the less stable conformer reveal that it is planar (C_{2v} symmetry, maximum possible dihedral angle 10–15°) in a wide range of matrix materials and is therefore properly referred to as *s-cis*-1,3-butadiene, at least in the condensed phase.

While the structure of the more stable s-trans conformer of 1,3-butadiene has been well established,[1] the structure of the less stable conformer has been a topic of discussion and dispute among both theoreticians and experimentalists. The focus of this has been the $C_1C_2C_3C_4$ dihedral angle: a planar 0° angle in an s-cis structure (C_{2v} symmetry) would maximize conjugation of the double bonds, while a gauche structure, with a dihedral angle intermediate between 0° and 90° (C_2 symmetry), would relieve steric strain between the inside hydrogens of the terminal methylene groups. The results of some calculations support a planar structure,[2] but most favor a gauche structure.[3] One of the most recent and therefore presumably most reliable calculations favors the gauche form,[3f] with a dihedral angle of about 38°, another favors a planar s-cis structure.[2c]

For many years experimental observations of this less stable conformer were rare, because of its low equilibrium concentration at room temperature.[4] A key advance in this area was the discovery[5] that hot butadiene vapor could be deposited with excess argon onto a very cold substrate, trapping the high-temperature equilibrium mixture and producing matrices rich in the minority conformer. This technique permitted the identification of the IR spectrum of this conformer. The frequencies and intensities, however, did not definitively distinguish between the possible C_{2v} and C_2 symmetries.

This same procedure was used to obtain the UV spectrum of the minor conformer,[5c] and an argument in favor of the planar s-cis structure was based on it: the first $^1\pi\pi^*$ transition of the minority conformer (λ_{max} = 226 nm) lies well to the red of the first $^1\pi\pi^*$ transition of the s-trans isomer (λ_{max} = 212 nm), as would be expected from theory[6] for the planar (C_{2v}) form (ref 6b provides a discussion of the physical origin of this type of difference).

However, since small angles, α, of twist around the C_2–C_3 bond which produce a C_2 geometry change the π resonance integral of this bond only as cos α, they have only a small effect of the $^1\pi\pi^*$ excitation energy. Thus, while the UV evidence rules out very large twist angles (say, 60°), the published claim of a ± 15° limit[5c,e] may be somewhat optimistic, since the difference expected for the two planar forms is known from theory with only rather limited accuracy.

We now wish to point out that a simple polarized IR measurement places a limit on a deviation from planarity in a manner free of the theoretical uncertainty that burdens the UV argument. Our results support the s-cis assignment obtained from the UV spectra and place better defined limits on the possible deviations from planarity. We have repeated our measurements in different matrix materials, in order to rule out a possible matrix packing bias in any particular environment. We find C_{2v} symmetry in all matrices tested and conclude that the minority conformer of 1,3-butadiene exists in the s-cis form in condensed phase.

The results demonstrate the utility of the simple, widely applicable technique of polarized IR spectroscopy in answering fundamental conformational questions.

Experimental Section

Materials. 1,3-Butadiene (Matheson C.P., 99.0%) was used without purification and showed no impurities in the IR. Argon (Matheson, UHP, 99.995%), nitrogen (Matheson, UHP, 99.999%), neon (Cryogenic, 99.999%) and methane (Matheson, Tech) were used without purification and showed no impurities in the IR.

Procedure. A 1:1000 mixture of butadiene in the matrix material, or neat butadiene, was passed through a quartz tube oven (1-cm i.d. × 10 cm) at 900 °C and deposited onto a 20 K CsI window. Flow rates were about 0.03 mmol of butadiene/h, and deposition times were about 30 min. IR spectra were recorded at 1-cm^{-1} resolution by using a Nicolet 6000 series FT-IR spectrometer and an IPG-225 aluminum grid polarizer (Cambridge Physical Sciences, Ltd.). Irradiation at 248 nm with a Lambda Physik EMG 100–201 KrF Excimer laser through a Wollaston polarizer produced partially oriented solid solutions in about 300 pulses. Complete conversion was accomplished with 5000 pulses of unpolarized irradiation.

Results and Discussion

General. Polarized absorption measurements capitalize on the fact that every UV or IR transition is characterized not only by its energy and intensity but also by a particular direction in the molecular framework, known as its polarization direction.[7] In

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Table I. Orientation Factors K of IR Transition Moments in the Minor Conformer of 1,3-Butadiene

				matrix[d]				
$\bar{\nu}$, cm^{-1}[a]	$\bar{\nu}$, cm^{-1}[b]	assignment[c]	polarization[a,c]	argon	neon	methane	neat	nitrogen
1828	1828	combination	x	0.251	0.240	0.242	0.227	0.280
1632	1632	C=C stretch	x	0.247	0.246	0.239	0.223	0.284
1612	1612	C=C stretch	yz	0.380	0.376	*e*	0.385	0.367
1425	1425	CH_2 scissors	yz	0.366	0.379	0.411	0.391	0.374
1402	1402	CH_2 scissors	x	0.249	0.239	*e*	0.230	0.278
1089	1089	CH_2 rock	x	0.246	0.241	0.241	0.288	0.287
995	995	CH bend	yz	0.372	0.372	0.407	0.382	0.366,[g] 0.368,[g] 0.367[g]
914	913	CH_2 wag	yz	0.377	0.385	*e*	0.395	0.351,[g] 0.364,[g] 0.365[g]
740	*f*	CH_2 twist	yz	0.373	0.374	*e*	*e*	0.359
601	600	C=C—C def	yz	0.370	0.383	*e*	0.384	0.378
K_x				0.249 ± 0.002[h]	0.242 ± 0.004[h]	0.241 ± 0.002[h]	0.227 ± 0.002[h]	0.282 ± 0.004[h]
$K_y = K_z$				0.373 ± 0.006[h]	0.378 ± 0.005[h]	0.409 ± 0.002[h]	0.387 ± 0.005[h]	0.367 ± 0.007[h]
ϕ[i]				13°	11°	6°	9°	17°

[a] This work. [b] Reference 5c. [c] Reference 3f. [d] 12 K except for neon, 5 K. [e] Band obscured in this matrix. [f] Not reported in ref 5c. [g] K values for the three observed sites. [h] Standard deviation. [i] Maximum deviation from orthogonality to x.

order to utilize a polarized IR measurement, a partially aligned solution is needed. This can be obtained by using an anisotropic solvent such as stretched polyethylene[7,8] or by using the anisotropic properties of light. The latter technique, known as photoselection,[7,9] is applicable whenever the solute is capable of undergoing a phototransformation. In the present case, photoselection on the minor conformer of 1,3-butadiene is possible since it photoisomerizes to the trans conformer.[5c] The absorbing UV transition moment of the first $\pi\pi^*$ transition is directed along the line connecting C_1 with C_4. Thus, those molecules of the initially randomly oriented minor conformer in the deposited sample, whose C_1–C_4 axes are lined up approximately parallel to the electric vector direction Z of the linearly polarized UV light, will have higher absorption probability and will be preferentially depleted in a partially photobleached sample.

Quite a few polarized IR measurements on matrix-isolated molecules partially oriented by photoselection have been reported over the last decade or so[10] but usually without an attempt at a quantitative evaluation. Techniques for such quantitative evaluation have been available from work on solutes oriented in stretched polymers, initially primarily in the UV region[7,11] but more recently increasingly in the IR as well.[7,8] Recently, these quantitative evaluation techniques have begun to be applied to photoselected matrix-isolated samples.[12] A detailed description of the procedures used is available elsewhere,[7,8,11,13] here, we shall only outline them briefly.

The alignment of a sample due to photoselection with linearly polarized light whose electric vector lies along the laboratory axis Z is uniaxial with Z as the unique axis and X and Y equivalent. A description of such alignment adequate for the analysis of linear dichroism is provided by the three orientation factors of eq 1–3,

$$K_x = \langle \cos^2 \underline{x} \rangle \qquad (1)$$

$$K_y = \langle \cos^2 \underline{y} \rangle \qquad (2)$$

$$K_z = \langle \cos^2 \underline{z} \rangle \qquad (3)$$

$$K_x + K_y + K_z = 1 \qquad (4)$$

where x, y, and z are the principal axes of the orientation tensor in the molecular frame, $\underline{x}$, $\underline{y}$, and $\underline{z}$ are the respective angles that these axes make with Z, and the pointed brackets indicate ensemble averaging. For a uniaxial distribution of the molecules remaining after a partial photodestruction by Z-polarized light absorbed by a UV transition purely polarized along x, it can be shown that $K_x < K_y = K_z$, where the y and z directions can be chosen arbitrarily as long as x, y, and z are all mutually orthogonal. It is normally advantageous to choose y or z or both to coincide with the symmetry axes of the molecule, if they exist.

All IR or UV transitions polarized along the axis u ($u = x, y, z$) will show the dichroic ratio

$$d_u = E_Z(u)/E_Y(u) = 2K_u/(1 - K_u) \qquad (5)$$

as long as they do not overlap (or if a suitable correction for overlap is made[11]). Here $E_Z(u)$ and $E_Y(u)$ are the Z-polarized and the Y-polarized absorbance, respectively, measured at the frequency of a u-polarized transition.

In molecules containing symmetry elements, transition moments of nondegenerate transitions have to be either parallel to a molecular axis of rotational symmetry or perpendicular to it. Also, they must either lie in a symmetry plane or be perpendicular to it. Exceptions are possible only if strong interactions with a low-symmetry environment effectively reduce the symmetry of the chromophore.[14]

As a result, in molecules of relatively high symmetry, such as C_{2v}, each transition has to be polarized along one of the symmetry axes x, y, or z so that the only two possible distinct orientation factors will be K_x and $K_y = K_z = (1 - K_x)/2$ and the only two possible dichroic ratios will be d_x and $d_y = d_z$. Note that for this type of uniaxial orientation distribution, a single measurement of d_x or d_y is sufficient to determine both K_x and $K_y = K_z$.

In molecules of lower symmetry, such as C_2 or C_{2h}, other polarization directions are possible. For these, the orientation factors K_ϕ of a general transition will differ both from K_x and from $K_y = K_z$, and we have $K_x \leq K_\phi \leq K_y = K_z$. If the transition moment makes an angle ϕ with x, the orientation factor for this transition will be

$$K_\phi = K_x \cos^2 \phi + K_y \sin^2 \phi \qquad (6)$$

Thus, an observation of more than two different orientation factors, or the observation of two different orientation factors unrelated by $K_y = (1 - K_x)/2$, is sufficient to demonstrate that effective

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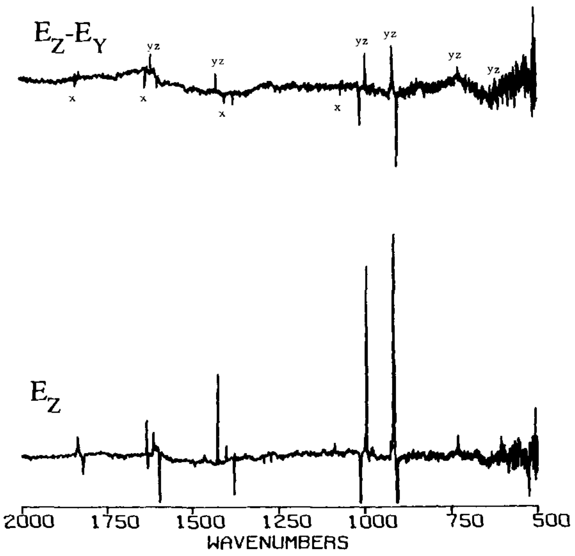

Figure 1. FT-IR spectra of *s-cis*-1,3-butadiene matrix-isolated in argon. In E_Z (E_Y), the electric vector of the observing beam is parallel (perpendicular) to the electric vector of the photoorienting beam. Bottom: Difference spectrum of partially photoconverted and fully converted sample. Peaks of the s-cis conformer are positive; those of the s-trans conformer are negative. Top: Difference of parallel and perpendicular polarized spectra of a partially aligned sample, labeled with transition-moment directions (see Table I). Unmarked peaks are due to the oriented trans conformer.

molecular symmetry cannot be as high as D_{2h}, or C_{2v}, as long as transition overlap can be excluded or corrected for. The value of K_ϕ can then be used to determine the angle ϕ provided that K_x and $K_y = K_z$ are known (eq 7). In the absence of strong solvent–solute interactions, the effective molecular symmetry will be that of the molecule itself.

$$\phi = \tan^{-1} [(K_\phi - K_x)/(K_y - K_\phi)]^{1/2} \qquad (7)$$

Minor Conformer of Butadiene. The IR bands attributable to the two conformers of 1,3-butadiene are readily apparent in the difference IR spectrum (Figure 1, bottom). This spectrum is the result of subtracting the IR spectra of the matrix-isolated sample deposited from the hot oven before and after irradiation with 248-nm light. Long irradiation at this wavelength quantitatively converts the minority isomer into the trans material.

When Z-polarized 248-nm light is used on an argon matrix-isolated sample, all the bands of the remaining minority isomer are dichroic (Figure 1, top). At a particular degree of conversion, their orientation factors were calculated from the measured dichroic ratios by using the relation $K_u = d_u/(2 + d_u)$. They are listed in Table I for the partially photoconverted argon-isolated sample along with the observed frequencies and the results of recent calculations.[3f] Only two distinct values of K_u are observed: 0.249 ± 0.002 and 0.373 ± 0.006. The smaller value, 0.249, corresponds to K_x, and all vibrations that share this value are polarized along the $\pi\pi^*$ transition moment, approximately (or exactly) along the C_1–C_4 line. For the remaining orientation factors we expect $K_y = K_z = (1 - K_x)/2 = 0.3755 \pm 0.001$, and this lies within experimental error of the other observed value, 0.373 ± 0.006. This implies that all of the transition moments that do not lie in the x axis lie perpendicular to it, i.e., in the yz plane. From the experimental error limits of the argon matrix data, we estimate from eq 7 that the maximum possible deviation of any of the observed transition moments from the x, y, or z axis is 11–13°. When the irradiation is interrupted at another degree of conversion, different K_x and $K_y = K_z$ values result, but they again add up to unity, and the same conclusion can be drawn.

The observed restriction of all observed IR transition moments to either the x direction, approximately or exactly parallel to the C_1–C_4 line, or the yz plane could in principle be accidental. This strikes us as unlikely in view of the fairly large number of these transitions. It appears much more probable that the restriction results from the presence of a symmetry element in the molecule. Judging by the photoselection results above, this could be a rotational axis of symmetry directed along x or a mirror plane located in yz. Since 1,3-butadiene cannot have a rotational symmetry axis located anywhere near the C_1–C_4 line, we take the photoselection results to imply that yz is a symmetry plane of the minor isomer of 1,3-butadiene, so that the C_2 symmetry group is excluded. On the other hand, the observations agree perfectly with expectations for the C_{2v} group, in which all transition moments must lie along x, y, or z and thus be always mutually parallel or perpendicular.

Another confirmation of the C_{2v} symmetry of the minor conformer can be seen in the unobservably low intensity of those vibrations which belong to the a_2 representation in the C_{2v} group and thus are symmetry forbidden in *s-cis*-1,3-butadiene but allowed at a gauche geometry.

To demonstrate that the observed symmetry is in fact representative of the minor isomer of 1,3-butadiene and not an expression of the preferred packing geometry of the matrix, the experiment was repeated using N_2, Ne, and CH_4 as matrix materials and also on a neat deposition of the high-temperature mixture of 1,3-butadiene conformers. These results are also listed in Table I.

The conclusions are identical in all five cases, and the error limits permit a deviation of transition-moment directions of no more than about 10° from the orthogonal x, y, and z axes. This permits a dihedral angle of no more than 15°. In order to reach this conclusion, we have considered the angle between the transition moment of the antisymmetric CH_2 rock[15] at 1089 cm^{-1} and the C_1–C_4 direction, taken to represent the direction of the UV transition moment, as a function of the dihedral angle. This angle is 0° for the s-cis conformer and gradually increases to 70° upon rotation to the s-trans conformer.

The results for the N_2 matrix-isolated sample require further comment. Splitting of the out-of-plane vibrations is observed in the s-cis spectrum and the spectrum of the s-trans photoproduct. This splitting is attributed to a matrix effect and is indicative of molecules imbedded in different sites in the lattice. We note, however, that the K value is the same for each site and conclude that the C_{2v} symmetry is maintained in every one of the three different environments.

In effect then, we have obtained the same result in seven different environments, namely, planarity within at most 15°. This is unlikely to be a coincidence. It suggests that the minority isomer of 1,3-butadiene is indeed planar s-cis butadiene in any condensed environment.

The five samples analyzed above were oriented by photoconverting less than 50% of the sample. Working at a higher degree of conversion, it should be possible to further define the maximum deviation from planarity. In one very carefully done argon matrix experiment, in which about 90% of the 995-cm^{-1} *s-cis*-butadiene band was converted with polarized light, we were able to achieve a considerably better oriented sample. Under these conditions, only the 1425-, 1402-, 1089-, 995-, and 914-cm^{-1} bands could be accurately measured. The value of $K_y = K_z$ was now determined to be 0.443 ± 0.003 and K_x to be 0.114 ± 0.003. With the observed value of $K_\phi = 0.116$ for the 1089-cm^{-1} vibration, the maximum allowable dihedral angle is reduced to 9°. Clearly, the evidence points to a planar structure.

The question remains whether the C_{2v} geometry also represents a potential energy minimum of an isolated gas-phase molecule of the minor conformer. Strictly speaking, this can only be determined by measurements on isolated gas-phase molecules and cannot be extrapolated from information on molecules contained in condensed media. The fact that we can fairly confidently exclude special packing force effects since we obtain the same result in all environments does not yet mean that the stabilization by dispersion forces due to any condensed environment could not

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(15) Assumed equal to the vector sum of antisymmetrically disposed vectors located in the $C_1C_2C_3$ and $C_2C_3C_4$ planes and perpendicular to the C_1–C_2 and C_3–C_4 bonds, respectively.

always be sufficiently larger for the better conjugated C_{2v} molecule than for the C_2 geometry to overcome the inherent preferences of the solute molecule. In order to minimize the effects of dispersion forces, we have included a neon matrix in our investigations, but even then, the results were the same.

Since it is difficult to imagine that a small deviation from planarity will affect the dispersion forces dramatically, we consider it very unlikely, although possible in principle, that an isolated molecule of the minor conformer of butadiene is nonplanar.

This conclusion disagrees with some of the best currently available calculations[3f] and agrees with others,[2c] but it must be emphasized that the calculated potential energy surface is very flat with respect to the $C_1C_2C_3C_4$ dihedral angle and thus to C_2–C_{2v} interconversion, so that the exact location of the minimum is undoubtedly extremely sensitive to the quality of the calculation. Since the correction for the electron correlation energy is most likely largest at the planar geometry, it is conceivable that calculations incorporating a larger fraction of the correlation effects will indeed produce a minimum at C_{2v} geometry. If improved calculations on an isolated molecule continue to predict a nonplanar geometry, it would be interesting to perform calculations for *s-cis*-butadiene surrounded by Ne atoms or perhaps already for the van der Waals complex of *s-cis*-butadiene with a single neon atom.

Conclusions

We have shown, employing the relatively simple technique of polarized matrix-isolation IR spectroscopy, that the minor rotamer of 1,3-butadiene is in fact planar within at most 10–15° in a wide variety of matrix environments and, hence, should be called *s-cis*-1,3-butadiene. Although we consider it very likely that this also is the geometry of this conformer in the gas phase, in disagreement with some of the best calculations available, this has not been strictly proven.

More generally, we have demonstrated the applicability of quantitative polarized IR spectroscopy to basic questions of molecular conformation, and this may stimulate further interest in this potentially important tool, applicable among others to molecules that cannot be readily observed except in matrix isolation.

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Registry No. 1,3-Butadiene, 106-99-0.

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^{17}O NMR Spectroscopy: Torsion Angle Relationships in Aryl Carboxylic Esters, Acids, and Amides

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Abstract: ^{17}O NMR spectroscopic data (natural abundance in acetonitrile at 75 °C) were obtained for the following series of electronically similar, sterically hindered compounds: aromatic methyl esters (**1–10**), aromatic carboxylic acids (**11–19**), and aromatic amides (**20–29**). Torsional angles were calculated by the molecular mechanics (MM2) method. Linear regression analysis of the estimated torsion angles and the ^{17}O chemical shift data for each series yielded the following results (series, slope δ/degree, correlation coefficient): esters (C=O), 0.70, 0.997; esters (–O–), 0.43, 0.992; acids ($-CO_2H$), 0.56, 0.994; amides (C=O), 0.84, 0.942; *N,N*-dimethylamides (C=O), 0.6, 0.991. The results are discussed in terms of minimization of repulsive van der Waals interactions by rotation of the functional group out of the plane of the aromatic ring.

^{17}O nuclear magnetic resonance spectroscopy is rapidly developing into a valuable method for examining a wide variety of structural problems[1] and may provide new insights into understanding chemical reactivity.[2] Carboxylic acids and their derivatives are among the most widely used synthetically and the most intensively studied of all functional groups. However, ^{17}O NMR studies of this important class of functional groups are limited to electronic effect studies in homologous series[3] or tabulations of chemical shift data on isolated types of compounds.[4] Recent findings have shown that ^{17}O NMR data for aromatic nitro compounds correlate well with torsion angles (X-ray).[5] In addition, ^{17}O NMR data for aryl ketones show a reasonable correlation with torsion angles (estimated by molecular mechanics calculations).[6] Determination of the solution-phase geometry of carbonyl-type functional groups has been under investigation for many years.[7] Classical methods used to estimate solution-

Table I. ^{17}O Chemical Shift Data (±1 ppm) for Aromatic Esters in CH_3CN at 75 °C

compd	Ar–CO_2Me	δ (C=O)	δ (–O–)	torsion angle,[a] deg
1	Ph	340	128	2
2	4-MeC_6H_4	339[b]	127[b]	2
3	2-MeC_6H_4	359	138.5	29
4	2,3-$Me_2C_6H_3$	363	141	29
5	2,6-$Me_2C_6H_3$	377	150	54
6	2,4,6-$Me_3C_6H_2$	376	149	54
7	1-naphthyl	361	139	33
8	2-naphthyl	341	129	2
9	9-anthryl	385	154	67
10	2,4,6-*t*-BuC_6H_2	392	162	76

[a] Calculated by molecular mechanics method (MM2) (±2°). See ref 15. [b] from ref 3; taken in acetone at 40 °C.

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