# Structure of Matrix-Isolated *s-cis*-1,3-Butadiene from Polarized IR Spectra: A Closer Look

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Abstract: A re-examination of polarized IR spectra of the minor conformer of 1,3-butadiene isolated in argon matrix and partially aligned by photoselection confirms the previous conclusion that in weakly interacting solid environments this species is planar, i.e., s-cis, and not gauche as often believed.

There is not much experimental evidence on the long-controversial issue[1-8] of the equilibrium geometry of the minor conformer of 1,3-butadiene. In room temperature equilibrium, this species represents only about 3% of the conformer mixture[4] and direct observation is difficult. Much larger relative concentrations are available in low-temperature matrices, obtained either by deposition of hot vapor[2,3] or by photoisomerization of the major s-trans conformer.[3] The UV absorption spectrum of the matrix-isolated minor conformer was found to be considerably red-shifted relative to that of the major conformer and it was concluded[3] that the minor conformer cannot be strongly twisted and most likely is planar, i.e., s-cis (**1**). This UV absorption spectrum

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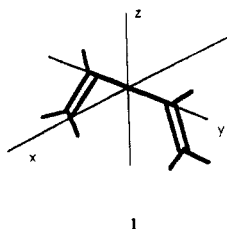
has since been questioned,[5] but we believe that it is basically correct. IR frequencies are compatible with either geometry;

stronger evidence on the point was obtained from polarized IR spectra of the matrix-isolated minor conformer oriented by photoselection.[6] All IR transition moments were found to be mutually parallel or perpendicular, as expected for a planar s-cis C_{2v} geometry but in general not for a nonplanar gauche C_2 geometry, except by accident. A simple estimate of the dependence of the transition moment directions on the dihedral twist angle and comparison with experimental uncertainties in the dichroic ratios suggested that the twist angle cannot differ from zero by more than 10-15°.

This conclusion has met with considerable skepticism, expressed mostly privately. The primary reason for the doubts has been the results of most,[7] though not all,[8] recent ab initio calculations that predict the gauche form, with a dihedral angle of 35-40°, to be more stable than the s-cis form by 0.5-1.0 kcal/mol. In one critical comment that has appeared in print,[7b] additional points were raised. One of these is relevant for our conclusions concerning the planarity of the minor conformer, has been raised in other papers as well,[7c] and has been of some concern to us, too: a 730-cm^{-1} vibration that is symmetry-forbidden in the planar C_{2v} form (a_2 symmetry) appears in the matrix IR spectrum, presumably due to an environmental perturbation.

In view of these doubts, we have decided to re-examine the issue. We have repeated all of the experiments, using a new and more accurate FT-IR spectrometer, and extended them to the C-H stretching region. In place of simple qualitative arguments, we have used ab initio MP2 calculations with a 6-31G* basis set to obtain information on the expected transition moment dependence on the dihedral angle. We now report the results of this reinvestigation.

Experimental Section

In all experiments 1,3-butadiene (Matheson, C.P., 99.0%) and argon (Matheson, UHP, 99.999%) were used as received and showed no impurities in the IR.

For the pyrolytic generation of the minor conformer a 1:5000 mixture of butadiene in Ar was passed through a quartz tube oven (0.9 cm i.d. × 10 cm) at 1100 K and deposited onto a CsI window at 28 K. Flow rates of about 0.02 mmol butadiene per hour and deposition times of 20 min were used.

For the photolytic generation of the minor conformer a 1:5000 mixture of butadiene in Ar was deposited directly onto a CsI window at 28 K. An elemental Zn lamp (Philips 93106E E27) irradiated the matrix during the deposition.

Partially oriented solid solutions were obtained by irradiation of the matrices with 248-nm light from a Lambda Physik EMG-50 excimer laser or with the filtered and collimated light from elemental lamps, 227 and 229 nm from a Cd lamp (Philips 93107E E27) and 254 nm from a Hg lamp (Philips 93123E E27), that had been linearly polarized along the laboratory Z axis by passing through a Glan-Thompson or a Wollaston polarizer.

The IR spectra were recorded on a Nicolet 60 SXR FT-IR spectrometer at 1 cm^{-1} resolution. A IGP-225 polarizer (Cambridge Physical Sciences) was used to measure polarized spectra.

The dichroic ratios (Table I) were determined by measurement of peak intensities polarized parallel and perpendicular to the laboratory Z axis. Estimates of the peak intensities were obtained by spectral subtraction, measurement of peak areas by integration, and measurement

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Table I. Normal Mode Vibrations of s-cis-1,3-Butadiene

		observed			calculated					
					planar			gauche		
i	$\bar{v}$	d_u	pol.		$\bar{v}$	pol.		$\bar{v}$	pol.	
1	3035	1.06 ± 0.01	xz	b_1 or a_1	3312	z	a_1	3312	z	a
2	3023	1.07 ± 0.01	xz	b_1 or a_1	3228	z	a_1	3223	z	a
3	2990	1.07 ± 0.01	xz	b_1 or a_1	3217	z	a_1	3211	z	a
4	1602	1.05 ± 0.01	xz	b_1 or a_1	1706	z	a_1	1712	z	a
5	1425	1.098 ± 0.005	xz	b_1 or a_1	1515	z	a_1	1510	z	a
6					1392	z	a_1	1369	z	a
7					1092	z	a_1	1099	z	a
8					907	z	a_1	931	z	a
9	596	1.088 ± 0.005	xz	b_1 or a_1	309	z	a_1	278	z	a
10	984	1.083 ± 0.005	xz	b_1 or a_1	1018		a_2	1019	z	a
11	920	1.083 ± 0.005	xz	b_1 or a_1	907		a_2	915	z	a
12	730	1.093 ± 0.005	xz	b_1 or a_1	739		a_2	763	z	a
13					165i		a_2	186	z	a
14	996	1.083 ± 0.005	xz	b_1 or a_1	1041	x	b_1	1041	xy	b
15	914	1.083 ± 0.005	xz	b_1 or a_1	921	x	b_1	932	xy	b
16	470	1.074 ± 0.005	xz	b_1 or a_1	520	x	b_1	471	xy	b
17	3103	0.88 ± 0.01	y	b_2	3309	y	b_2	3310	xy	b
18	3070	0.88 ± 0.01	y	b_2	3219	y	b_2	3218	xy	b
19	3010	0.85 ± 0.01	y	b_2	3206	y	b_2	3203	xy	b
20	1633	0.857 ± 0.005	y	b_2	1721	y	b_2	1716	xy	b
21	1403	0.883 ± 0.005	y	b_2	1480	y	b_2	1476	xy	b
22					1343	y	b_2	1336	xy	b
23	1087	0.883 ± 0.005	y	b_2	1136	y	b_2	1125	xy	b
24	530	0.861 ± 0.005	y	b_2	570	y	b_2	632	xy	b

of peak heights. All three methods agreed within the experimental uncertainties listed.

Calculations. Ab initio calculations were carried out at the MP2 level with the standard 6-31G* (6d) basis set. Analytical procedures were used to determine the minimum energy geometries, vibrational frequencies, IR intensities, and IR transition moment directions. Strictly speaking, these procedures should not be used at geometries other than those of potential energy surface extrema, since the Eckhart conditions then need not be fulfilled. We have used them also at certain geometries with a very small but non-zero gradient and assume that the error introduced is negligible relative to others already present. All calculations were carried out on a Cray XMP/24 computer with the CADPAC[9] program.

Results

Argon-matrix isolated samples of 1,3-butadiene (1:5000) enriched in the minor conformer were obtained either by deposition through an 1100 K oven or by 214-nm irradiation of matrices containing mostly the major conformer. Irradiation at 248 nm (pulsed) and 227 and 229 or 254 nm (continuous wave) rapidly converts the minor into the major conformer. From an increase in the IR peaks of the major conformer upon complete photo-destruction of the minor conformer, we estimate that the oven-deposited samples contain about 20% and those obtained with 214-nm radiation about 60% of the latter. Identical results were obtained starting with either type of sample. No interference was observed from the additional photoproducts that are formed in the 214-nm irradiation of the major conformer and are detected in the IR spectrum.

Photoalignment of the matrix-isolated minor conformer was accomplished by irradiation with pulsed 248-nm or continuous wave 227- and 229-nm or 254-nm light linearly polarized along the laboratory Z axis, with identical results. The previously reported behavior[6] was reproduced exactly. The IR of the remaining minor conformer gradually becomes dichroic, and the degree of dichroism increases until there is so little of the minor conformer left that its IR can no longer be observed reliably. The superior sensitivity and photometric accuracy of the presently used FT-IR spectrometer permitted us to follow the process to higher degrees of conversion, reduced the error bars on the dichroic ratios, and permitted an extension of the measurements to the whole region from 400 to 4000 cm⁻¹. At all degrees of photoconversion, the dichroic ratios of all the vibrations, including the C-H

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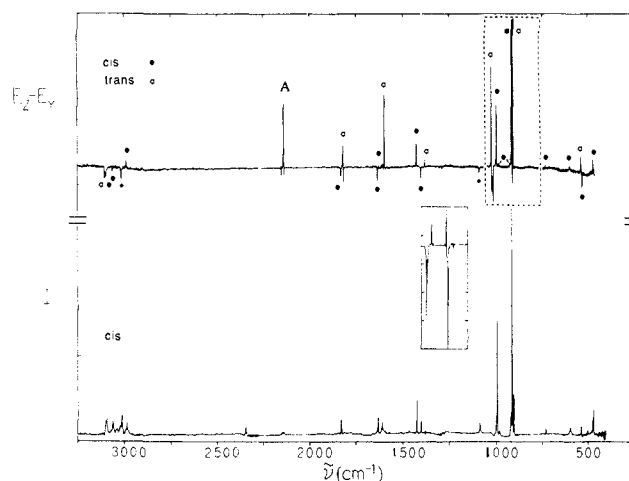

Figure 1. Bottom: isotropic IR spectrum of s-cis-1,3-butadiene in argon at 10 K obtained as the difference of the spectra before and after 248-nm irradiation of the products from a hot-vapor deposition. Top: difference between the polarized spectra of 1,3-butadiene in argon at 10 K, partially oriented by irradiation of a hot-vapor deposit with linearly polarized 248-nm light. The peak labeled A is a secondary photolysis product. The most intense peaks are distorted in the main spectrum and rendered correctly in the inset obtained by subtraction of polarized spectra with optical densities of 1 or less.

stretches, had only two distinct values. Table I lists the results for a particular measurement and the error margins. The difference E_Z - E_Y of the Z-polarized and Y-polarized absorbances at a particular degree of conversion is shown in Figure 1. This also shows an ordinary (unpolarized) spectrum (E^{iso}) of an unoriented sample of the minor conformer, in which peaks due to the major conformer have been subtracted by computer. The fact that in the difference spectrum E_Z - E_Y of the oriented sample all the positive peaks have the same dichroic ratio (0.350) and all the negative peaks have the same dichroic ratio (0.304) is immediately apparent from the equality of the relative intensities within each group to those observed on the unoriented sample.

The dichroic ratio d_i of the ith IR peak is related to the orientation factor K_i of the ith transition moment by[10]

$$K_i = \langle \cos^2 i \rangle = d_i/(d_i + 2)$$

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where i is the angle between the i-th transition moment and the laboratory axis Z and the pointed brackets indicate ensemble averaging. The π–π^* transition moment responsible for the UV absorption by the minor conformer is certainly perpendicular to its 2-fold symmetry axis and essentially parallel to its C_1–C_4 direction. From the principles of photoselection,[10] this direction (y) will represent the "depletion axis", i.e., it will have the smallest orientation factor K_y in the partially aligned sample of the remaining minor conformer. The value of K_y is smaller than $^1/_3$, since on the average the y axis is inclined away from the direction Z of the electric vector of the UV light. This is immediately apparent when one considers that those molecules whose y axis is included toward Z are the most likely to absorb and are therefore most rapidly depleted by conversion to the major isomer.

If the UV absorption is purely polarized, i.e., in the absence of spectral overlap, all molecular axes perpendicular to the C_1–C_4 depletion axis y are equivalent with respect to the photoselection process and will have equal orientation factors, larger than $^1/_3$ and equal to $(1 - K_y)/2$. This equality follows from the properties of direction cosines in orthogonal axes ($K_x + K_y + K_z = 1$). We can arbitrarily select two such mutually orthogonal axes, and label them x and z. If possible, it is convenient to choose them in such a way that they either coincide with molecular axes of rotational symmetry or are perpendicular to molecular planes of mirror symmetry.

If the molecule has IR transition moments that are perpendicular to y, they will have the orientation factors $K_x = K_z = (1 - K_y)/2$ and will show the corresponding dichroic ratio $d = 2K_z/(1 - K_z)$. Transition moments whose directions make a general angle φ with the y direction will have orientation factors K_φ given by[10]

$$K_\varphi = K_y \cos^2 \varphi + K_z \sin^2 \varphi$$

There is general concensus[1,2] on which vibrations of the minor conformer are totally symmetric, i.e., which ones have transition moments along the 2-fold symmetry axis z. In all of our experiments, regardless of the degree of depletion, we observe the same orientation factor for all of them (labeled a_1 in Table I). Its value exceeds $^1/_3$ and this in itself implies that the angle between the 2-fold symmetry axis z and the UV-absorbing moment direction y is larger than the magic angle, 54.5°. Since from molecular symmetry it must be 0° or 90°, it is obviously 90° as already anticipated above. The orthogonality of the UV-absorbing transition moment to the molecular symmetry axis z surely is no surprise and in itself says nothing about the dihedral twist angle.

Regardless of the dihedral angle, the transition moments of all non-totally symmetric allowed IR vibrations must also be orthogonal to z. Those that show positive dichroism, i.e., make at least an angle of 54.5° with the y direction, are observed to have the same dichroic ratio and orientation factor as the totally symmetric vibrations (Table I). This means that they are orthogonal not only to z but also to y. Finally, the orientation factor K_y of all the IR vibrations that show negative dichroism is again the same, and it satisfies the condition $K_y = 1 - 2K_z$ at all degrees of depletion. This demonstrates that the transition moments of this third group of vibrations are all mutually parallel and directed along the UV-absorbing direction y.

In summary, the minor conformer has three classes of vibrations, polarized along mutually perpendicular directions, one of which coincides with the polarization direction of the UV transition. This is exactly the situation that would be enforced by symmetry if the dihedral twist angle were zero. For non-zero dihedral angles, there would be only two classes of vibrations. Those polarized in the 2-fold symmetry axis (z) would have transition moments orthogonal to all the others, and to the UV polarization direction. All the remaining vibrations would be free to assume polarization directions at some arbitrary angles with respect to one another and with respect to the UV transition moment direction y. We would then observe a common dichroic ratio and orientation factor

K_z for totally symmetric (a) vibrations and a series of values ranging from K_x to K_y for non-totally symmetric (b) vibrations. Such a multitude of in-plane polarization directions for the IR vibrations is indeed observed for the major conformer of 1,3-butadiene, which is of C_{2h} symmetry.[11] Although there is no a priori reason to expect anything else for the general gauche form of the minor isomer, it is obvious that for sufficiently small dihedral twist angles the arrangement of the transition moments that are perpendicular to z must become experimentally indistinguishable from that expected for the planar s-cis form.

The error margins with which we have been able to determine the angles between x-polarized and y-polarized IR transitions are dictated by the accuracy of the measured dichroic ratios and amount to ±10°. The question then is, how far could the planar s-cis conformer be twisted before a deviation from orthogonality would be detected? To obtain an answer, we need to estimate the transition moment directions of the non-totally symmetric vibrations as a function of the dihedral twist angle.

In a previous study, we have estimated this dependence in a simple empirical way, using vector addition of local contributions. We have now proceeded to compute them in the harmonic approximation at the ab initio MP2/6-31G* level. At this level, the calculations produce a reasonable if imperfect agreement for transition frequencies and reproduce well the IR transition moment directions in the major conformer, s-trans-butadiene[11] (Figure 2). Only the transition moment of ν_{18} agrees poorly. The agreement would be fine if we took the opposite sign for the experimentally undetermined angle of deviation of the transition moment from the C_1–C_4 axis. However, larger basis set calculations for s-trans-1,3-butadiene (MP2/6-311G**) dictate the sign shown.[11]

The results agree quite well with the previously employed[6] simple approach. At the MP2/6-31G* level of calculation, the s-cis-1,3-butadiene geometry corresponds to a saddle point with one imaginary frequency and the minimum in the potential energy surface occurs at a twist angle of 38°. The normal modes and transition moments were computed for this geometry first. Subsequent calculations were performed at geometries for which a dihedral value was imposed and all other geometrical parameters optimized. The transition moment computed for the twisting motion mode is then of little value, but all the others should be good approximations to the transition moments the molecule would have at that particular value of the dihedral angle, since the twisting coordinate appears to be nearly perfectly decoupled from the others. This is not surprising, considering that the computed potential energy surface is extremely flat along the twisting coordinate (within 1 kcal/mol between 0° and 60° twist) and much steeper in all other directions. The computed vibrational frequencies change by less than 20 cm^{-1} as a function of the assumed dihedral angle, except for ν_{16} and ν_{24}, which gradually shift by about 200 cm^{-1} as the dihedral angle goes from 0° to 180°. Such absence of coupling between the twisting and other motions was assumed in the earlier study.[6] Even so, the transition moment directions are affected quite strongly as the dihedral angle changes, since they reflect molecular geometry in a very sensitive fashion.

The results of the calculations of transition moment directions as a function of dihedral twist angle are shown in Figure 2. The twist angle is plotted radially, from 0° (s-cis, center) to 180° (s-trans, perimeter). The transition moment directions for all vibrations polarized perpendicular to the C_2 symmetry axis z, which is preserved during rotation about the C_2–C_3 bond, are plotted as the angular variable, with the vertical line representing the direction of the C_1–C_4 axis. To avoid congestion, only the orientation of one end of each transition moment vector is shown.

At 0° twist, the molecule has C_{2v} symmetry and the computed transition moments of all allowed vibrations polarized perpendicular to the C_2 axis lie along the C_1–C_4 axis or perpendicular to it, as they must. As the twist angle increases, the calculated transition moments are free to deviate from these two initial

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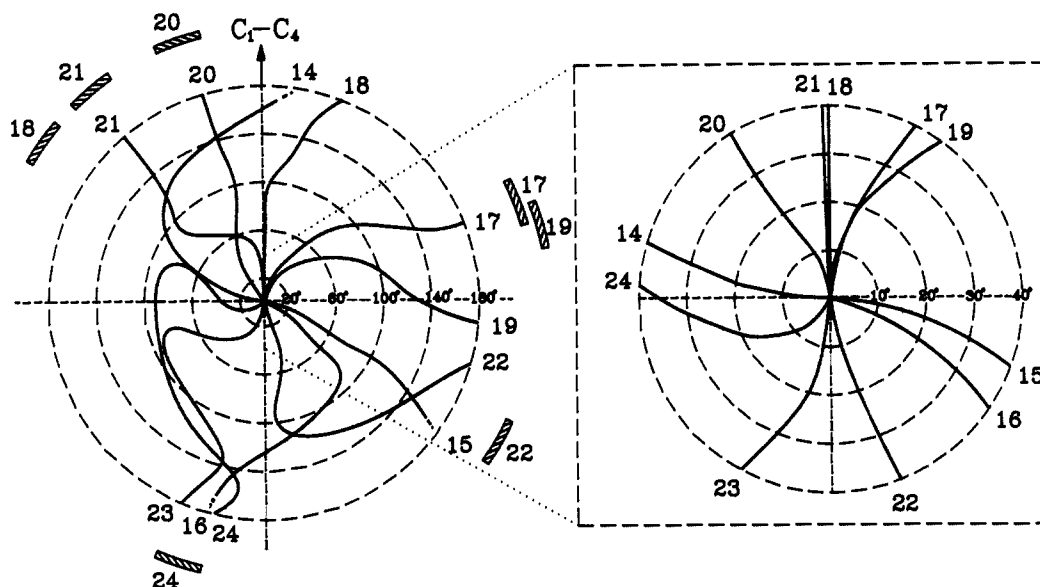
Figure 2. Computed (MP2/6-31G*) transition moment directions of b-symmetry normal modes of vibration of 1,3-butadiene as a function of the dihedral angle [radial coordinate, 0° (s-cis) at the center, 180° (s-trans) at the perimeter], shown with respect to the C_1–C_4 direction in the molecular framework, chosen vertical [angular coordinate]. C_2 is located to the right and C_3 to the left of the C_1–C_4 axis. The numbering of the vibrations is that of the s-cis conformer. The transition moments of those vibrations that acquire b_g symmetry vanish in the s-trans limit so that their direction is no longer defined (shown as dotted line ends). Measured[11] transition moment directions for s-trans-1,3-butadiene are shown by hatched arcs outside the perimeter; their length reflects experimental uncertainty.

directions, and Figure 2 shows that they do. In particular, the moments of ν_{16}, ν_{19}, ν_{20}, and ν_{24} deviate considerably already for twist angles as small as 10°. At this dihedral angle, the calculated transition moment directions are 73°, 10°, 19°, and 47° from the C_1–C_4 axis for ν_{16}, ν_{19}, ν_{20}, and ν_{24}, respectively. Since the measured dichroic ratios for these vibrations exclude the presence of deviations from orthogonality larger than ±10°, we conclude that the dihedral angle cannot be even as large as 10°, and probably is much less.

The calculation of the transition moments for the twist angle of 10° was repeated at the MP2/6-311G** level. The results are similar; the calculated transition moment directions of ν_{16}, ν_{19}, ν_{20}, and ν_{24} again deviate from the C_1–C_4 direction by angles significantly different from 0° and 90°: 78°, 21°, 22°, and 45°, respectively.

In order to illustrate the sensitivity of the IR dichroic measurements to the dihedral angle, we have synthesized the dichroic spectrum E_Z - E_Y that would be expected if the dihedral angle indeed were 38° as calculated (MP2/6-31G*), and if the transition moment directions were those calculated, assuming for simplicity that the direction y of the UV-absorbing transition moment lies exactly along the C_1–C_4 line. The result is clearly incompatible with what is actually observed, particularly for the vibrations near 500 and 3000 cm^{-1} (Figure 3).

If we accept the equilibrium geometry of the minor conformer to be C_{2v} (or within a few degrees of C_{2v}), the dichroic data do not provide an immediate classification of vibrations into a_1 (z-polarized) and b_1 (x-polarized), but this can be done quite reliably by comparison with the calculated frequencies and intensities. Overall, the assignment agrees well with those made previously.

The three vibrations of a_2 symmetry warrant further discussion. They are symmetry-forbidden in the C_{2v} point group, yet they appear with weak intensity in the matrix-isolated spectra. In the previous study,[6] several different matrix materials were employed. At the time, none of the three a_2 vibrations were observed in methane and neat butadiene matrices, while the one at 730 cm^{-1} was observed weakly in nitrogen and neon, and clearly in argon matrix, with a polarization perpendicular to the C_1–C_4 axis. As the presence of detectable intensity in the a_2 modes was one of the reasons why the initial report[6] met with skepticism,[7b,c] we have chosen argon for the present study, since it was most likely to exhibit deviations from planarity, if such are indeed manifested as a_2 absorption intensity. We have now looked very carefully and observed the 730-cm^{-1} vibration weakly in all of the above
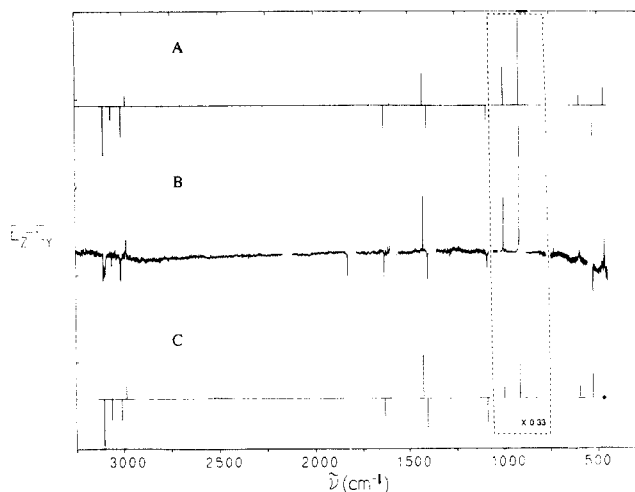
Figure 3. Observed dichroic IR spectrum E_Z - E_Y, with all non-minor conformer peaks eliminated, compared with those expected for two assumed dihedral angles for the minor conformer of 1,3-butadiene. (A) The expected spectrum if the minor conformer is planar. (B) The experimentally observed spectrum. (C) The expected spectrum of the minor conformer assuming a dihedral angle of 38° and the transition moment directions from a MP2/6-31G* calculation.

matrices (it is very broad in neat butadiene).

Since the polarized IR results are not compatible with a significant deviation from planarity, we attribute the appearance of non-vanishing a_2 intensity to matrix-induced mixing of fundamental modes. The appearance of symmetry-forbidden vibrations in matrix-isolation IR spectra is quite common. For instance, in the spectrum of the major conformer of 1,3-butadiene, several of the parity-forbidden a_g vibrations appear very clearly.[11]

Discussion

The results of polarized IR measurements reported presently for the minor conformer of 1,3-butadiene isolated in argon are only compatible with an essentially planar structure and thus confirm the conclusion reached previously[6] for seven different matrix environments. They also extend the assignments of the vibrations of this species to the C–H stretching region. A total of 19 vibrations of this conformer have now been identified and symmetry-assigned; of the five missing, the low-frequency twisting

mode is the most intriguing. The observed frequencies and relative intensities agree quite well with those calculated at the MP2/6-31G* level, except that almost all the frequencies are overestimated, as usual. However, the extremely flat energy profile computed for the twisting motion apparently has its minimum at the wrong position, 38° instead of 0° twist.

This could simply be due to the approximate nature of the calculation. For instance, inadequacies in the evaluation of correlation energy might vary with the dihedral angle and the resulting extent of π-conjugation. However, it is perhaps more likely that the problem lies elsewhere: the experiments are performed in condensed phase, and the calculations are performed for an isolated molecule and neglect the energy of solvation. The experimental result is independent of the exact nature of the solid environment and probably reflects the intrinsic preferences of the molecule in a compact and polarizable medium, rather than the packing preferences of the matrix material. Perhaps the planar molecule is sufficiently more polarizable and its van der Waals stabilization sufficiently greater to move the shallow minimum in the potential energy surface to 0° dihedral angle.

Two other possibilities to reconcile the results of the calculations with the experimental findings have occurred to us, but neither is very appealing. The first would be to postulate that the molecule

tunnels rapidly on the IR time scale between the two mirror-symmetry related gauche forms corresponding to the computed dihedral angles of +38° and −38°. The second possibility is that the torsional barrier is so small that already the lowest vibrational level lies above it. This is unlikely, since the calculated value of $h\nu/2$ for this mode is only 90 cm^{-1}, while the calculated barrier height is 319 cm^{-1}.

Either way, the computed potential energy minimum could still be at 35–40° yet the IR spectrum of the molecule would effectively correspond to a C_{2v} overall symmetry. In both cases, the molecules would have to be packed very inefficiently and be accommodated in quite large cavities in the matrix in order to permit large-amplitude motions. This strikes us as unlikely, given that the results are the same in seven different matrix environments.

We conclude that a correct reproduction of the quite inescapable experimental finding, a planar or nearly planar s-cis-1,3-butadiene in a variety of matrix environments, remains as an interesting challenge for structural theory.

The Minimal Permanganate Oscillator and Some Derivatives: Oscillatory Oxidation of $S_2O_3^{2-}$, SO_3^{2-}, and S^{2-} by Permanganate in a CSTR[1]

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Abstract: Oscillatory behavior is reported in the permanganate oxidation of several species in the presence of KH_2PO_4 in a stirred tank reactor. With Mn^{2+} as the reductant and NaOH added to maintain the proper pH, the resulting system is the "minimal permanganate oscillator," which serves as a core from which other oscillating permanganate reactions can be generated. In one example, discussed in detail, the manganous ion and NaOH are replaced by thiosulfate ion and H_2SO_4, respectively. Other permanganate oscillators contain sulfite or sulfide ions as the reductant. The phosphate serves both as a stabilizer of soluble Mn(IV) and as a pH buffer.

Oscillatory behavior is found in a wide range of enzyme-catalyzed reactions, and transition metals play a major role in the functioning of the enzymes involved in these processes. In view of this fact and the multiplicity of oxidation states available to many transition metals, compounds of these elements seem ideal candidates to serve as starting points for new chemical oscillators. It is therefore surprising that the first chemical oscillator based on transition-metal chemistry has only recently been reported. This system, the $KMnO_4$–H_2O_2–H_3PO_4 reaction in a flow reactor (CSTR), was discovered by Nagy and Treindl.[2] It was soon followed by reports of two more permanganate oscillators, the $KMnO_4$–ninhydrin–H_3PO_4[3] and the $KMnO_4$–KNO_2–formic acid–methanol[4] systems.

In a recent communication,[5] we presented initial results on a new and simpler permanganate oscillator, the Guyard[6] reaction of Mn^{2+}, MnO_4^-, and phosphate at near neutral pH in a CSTR. We referred to this system as the "minimal permanganate oscillator". A minimal oscillator in a family of oscillatory reactions

may be defined[7] as that oscillator containing components that are found in all members of the family as reactants or are generated during the reaction, and from which no component can be removed without destroying the ability of the system to oscillate. Since all permanganate–substrate reactions lead to manganese(II), and the phosphate is essential for oscillation, the Mn^{2+}–MnO_4^-–phosphate system is the minimal member of the family of MnO_4^-–reductant–phosphate oscillators, of which the first two examples[2,3] contain hydrogen peroxide and ninhydrin as the reductant.

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