periments would further exploit the structured spectra and nonnegligible fluorescence yields of our model Schiff bases. Neither of these advantages is found in rhodopsin.

The relative positions of the “$2^1B_u^{+}$” and “$1^1A_g^{-}$” states should influence the mechanisms by which rhodopsin disposes of its absorbed photons. Previous models of the 11-cis→trans isomerization have relied on excited-state potential surfaces calculated for a lowest excited singlet of “^1B_u” character.[4,27,47,48] Since the distribution of electrons is predicted to be much different in “$2^1A_g^{-}$”, the applicable potential energy surfaces (e.g., those describing the torsion about the bond corresponding to C_{11}–C_{12} in retinal) may lead to qualitatively different photochemical events. Our work indicates that the nature of rhodopsin's first excited state is, at least from an experimental point of view, very much an open question.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and a DuPont Fund grant to Bowdoin College for support of this research. We thank John Karris for developing the procedures used in obtaining corrected spectra, Steven Landau for the preliminary trichloroacetic acid protonation results, and Professors R. Birge and B. Hudson for helpful discussions.

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(47) Warshel, A. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 2558.
(48) Lewis, A. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 549.

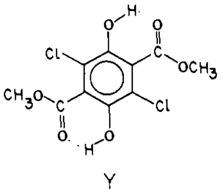
Spectroscopic Studies of the Thermal Rearrangement Reaction of Dimethyl 3,6-Dichloro-2,5-dihydroxyterephthalate in the Solid State

Jacek Swiatkiewicz† **and Paras N. Prasad***

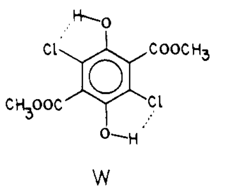
Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received March 29, 1982

Abstract: The thermal rearrangement of the yellow (Y) isomer of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate in the solid state, which yields a white (W) isomer, has been investigated by a combination of Raman phonon spectroscopy and electronic emission spectroscopy. The rearrangement is found to start as a homogeneous process but becomes heterogeneous as the product forms. The Raman spectra of the Y and the W isomers both in the phonon and in the internal vibration region show differences that relate to the difference in the nature of the hydrogen bonds of these two isomers in the solid state. A rigid-motion analysis of the published X-ray thermal parameters has been used to make assignments of the molecular nature of the phonon transitions observed in the Raman spectra. A temperature-dependence study of the Raman phonon spectra suggests that the rearrangement may be defect controlled rather than phonon assisted.

The thermal rearrangement of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate, which leads to the conversion of a yellow crystal to a white crystalline form, was reported by Hantszch[1] in the beginning of this century. This rearrangement process in the solid state was more thoroughly investigated by Curtin and Byrn[2] and by Byrn, Curtin, and Paul.[3] They used the X-ray diffraction technique to determine the detailed crystal structures of both the yellow and the white crystalline forms. In solutions, this compound also exhibits yellow and white forms.[4] A yellow solution is obtained in weakly interacting solvents such as chloroform. On the other hand, a white solution results in a solvent like methanol, which forms strong hydrogen bonds. The spectroscopic studies of these solutions reveal an equilibrium between two limiting structures.[4] The two forms differ in the nature of the hydrogen bond. The Y form (yellow) involves a hydrogen bond to the carbonyl oxygen atoms at each end of the molecule. The W form (white) has two intramolecular hydrogen bonds to the chlorine atoms. The molecular structures of the Y and W forms in the solid state differ in the conformation of the carboxymethyl groups with respect to the benzene ring. They are coplanar in the Y form but are distinctly out of the plane of the benzene ring in the W form. In the solid state, the Y form still contains the hydrogen bonding, which is predominantly intramolecular and of a chelate type. A detailed structural analysis[3] of the W crystalline form, however, suggests a bifurcated hydrogen bond involving an intermolecular O–H···O bond and an intramolecular H···Cl bond. Since there are differences in both the molecular conformation and the nature of the hydrogen bond, the two forms have been classified as chemical isomers.[3]



Y



W

Although both isomers crystallize in the same space group, $P\bar{1}$, the unit cell of the Y isomer contains one one-half molecule per asymmetric unit while that of the W isomer contains two one-half molecules per asymmetric unit. In other words, the conversion of the Y form to the W form leads to a doubling of the unit cell. A closer inspection of the spatial arrangement of the W structures reveals that it can be generated from the Y structure if a considerably large reorientation of the molecule is assumed. Specifically, a reorientation of nearly 180°, of half of the molecules, around the Cl–Cl axis is required in addition to the conformational change.[3]

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† On leave from the Institute of Organic and Physical Chemistry, Technical University of Wroclaw, Poland.

(1) Hantszch, A. *Chem. Ber.* **1915**, *48*, 797.
(2) Curtin, D. Y.; Byrn, S. R. *J. Am. Chem. Soc.* **1969**, *91*, 1865.
(3) Byrn, S. R.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 890.
(4) Curtin, D. Y.; Byrn, S. R. *J. Am. Chem. Soc.* **1969**, *91*, 6102.

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The conversion rate is highly dependent on the temperature. At room temperature, both isomers are stable and can be stored for an indefinite period. In contrast, a quantitative conversion of the Y form at 140 °C can take place in only several minutes. The previous works[2,3] suggest that the thermal rearrangement of the Y isomer begins by a random nucleation of the product crystal phase within the parent lattice. The initiation of this transformation occurs within a broad range of temperatures, but, once nucleation occurs, the crystal of the Y isomer undergoes an irreversible rearrangement. A microscopic observation[3] of the transformation suggests a heterogeneous mechanism for this thermal rearrangement process.

Recently, a novel method of "phonon spectroscopy of solid-state reactions" has been introduced by this research group[5-8] to investigate the mechanism of, and the role of lattice motions in, solid-state reactions. The primary motivation for studying the thermal rearrangement of the Y form by phonon spectroscopy was derived from our interest in investigating if a large reorientation, assisted by phonons (intermolecular lattice vibration), was involved in this rearrangement process. We also wanted to use phonon spectroscopy to study if the reaction occurs by a homogeneous or a heterogeneous mechanism at the molecular level.

This work reports on the investigation of the thermal rearrangement of the Y isomer by a combination of Raman spectroscopy, electronic spectroscopy, and thermal-parameters analysis of the published X-ray data. The specific aims of the study are (i) to derive a molecular understanding of this rearrangement process, (ii) to study the role of hydrogen bonding in the rearrangement, (iii) to investigate the mechanism of the reaction (homogeneous vs. heterogeneous), and (iv) to examine the role of phonon motions in assisting the rearrangement.

Experimental Section

General Methods. The Raman, photoexcitation, and emission spectra were recorded on a SPEX double monochromator with holographic gratings (Model 14018) by using a 90° scattering geometry. The excitation source for the Raman spectra was either the 5145-Å line of an argon ion laser (Coherent Radiation Model CR-8) or the output of a tunable CW dye laser pumped by the argon ion laser. A 75-W xenon lamp and a monochromator (from S. A. Instrument Inc., Model H-20) were used together to provide excitations for the photoexcitation and the emission studies. To obtain spectra at elevated temperatures, we heated samples by a flow of warm nitrogen gas. The samples were encapsulated in a thin-wall glass capillary to prevent sublimation. To obtain temperatures between 90–290 K, we used a cold nitrogen vapor in the same experimental arrangement. The experiments at liquid helium temperatures were performed in a Janis research cryostat.

Material Preparation. The reaction of chlorine with 2,5-dicarbomethoxy-1,4-cyclohexanedione was carried out in glacial acetic acid, as recommended by Curtin and Byrn.[4] They used a concentrated solution of chlorine in acetic acid for this reaction. Instead, we used the chlorine gas itself. A mixture of obtained dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate and 3,6-dichloro-2,5-dicarbomethoxybenzoquinone was crystallized out and washed with ethanol. Recrystallization from chloroform yields a mixture that has an apparent melting point of 174 °C. This mixture was reduced with zinc to convert the quinone to dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate. The crude product, obtained after subsequent crystallizations from glacial acetic acid and chloroform, was purified by repeated sublimations. The sublimation yields a mixture of both white and yellow isomers (m.p. 178–179 °C, lit. m.p. 177–179 °C[1,4] and 181–183 °C[3]).

Solid-State Work. Single crystals were grown by a slow evaporation of the solvent from the solution. Chloroform and acetone were the most favorable solvents used to obtain the Y-isomer crystals. The yellow crystalline material transformed to the white-isomer crystals (powder) at various temperatures within a range of 120–140 °C. The single crystals of the W isomer were grown with methanol as a solvent. The best quality W-isomer single crystals were, however, obtained by a slow sublimation. The powder material was made by a careful crushing and grinding of the small crystals.

Table I. Analysis of the Observed Frequencies in the Raman Spectra of the Y and W Isomers as well as of the Corresponding Quinone[a]

	yellow isomer	white isomer	quinone
ν(C–H)	3042 (3040)	3058 (3054)	
ν(C–H)	3015 (3027)	3030 (3026)	
ν(C–H)	3010		
ν(C–H) in CH$_3$	2964 (2960)	2966 (2966)	2960
	2850 (2855)	2860 (2856)	
ν(C=O)	1682 (1673)	1718 (1717)	1732
ν(C=O)		1708	
ν(C=O)		1699 (1699)	1685
ν(C=C)	1595 (1584)	1597 (1598)	1636
	1527 (1514)	1575 (1565)	
δ(C–H) in CH$_3$	1448 (1446)	1452 (1450)	1440
		1440 (1435)	
β(O–H)	1343 (1327)	1368	-
β(O–H)	(1317)	1360 (1351)	-
ν(C–O)	1309 (1311)	1316 (1305)	1346
ν(C–C)	1200 (1200)	1188 (1187)	1243
ν(C–OH)	1060 (1058)	1054 (1055)	-
ϕ(CC)	960 (953)	958 (956)	937
		(946)	
ν(C–O–C)	913 (911)	905 (903)	878
		896 (896)	
ϕ(CC)	850	836 (826)	834
		(816)	
γ(O–H)	786 (783)	770 (768)	
		753 (751)	
		508	
ϕ(CC)	489 (481)	488 (487)	484
β(C–OH)	410 (400)		
β(C=O) + β(C–C)	402 (390)	388 (385)	380
		373	
β(C–Cl)	340 (338)	337 (335)	320
		333	
γ(C–Cl)	300 (299)	290 (286)	288
γ(C–OH)	253 (250)	253 (251)	-
		250	
ν(CO···HO)		224 (223)	
		215 (215)	
δ(C–C)	185 (182)	194 (193)	162
ν(CO···HO)		152 (150)	
δ(C=O)		129 (129)	118
ν(CO···HO)		112 (110)	
δ(C=O)		99 (99)	102
	99 (88)		
	80 (78)	79	
lattice modes		65	
		57	
L$_1$	43.9 (43)	51.5 (51)	
L$_2$	31 (31)	47	

[a] ν, stretching modes; β in plane bending; γ, out of plane bending; δ deformation mode; ϕ(CC), skeletal deformation of the benzene ring.

The dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate was deuterated in the 2,5 positions by a slow crystallization from CDCl$_3$ saturated with D$_2$O, which yielded a polycrystalline Y-isomer solid. The deuterated white isomer was obtained after a complete transformation of the yellow isomer at 140 °C.

Results and Discussions

Raman Study of the Yellow and White Isomers. The laser Raman spectra of both the yellow and white isomer crystals of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate were obtained for the entire vibrational frequency range. The observed vibrational frequencies for the crystals of the two isomers are listed in Table I. It can be seen that there is no gap between the internal modes and the external lattice modes (phonons). This feature complicates the assignments of various modes. In order to derive assistance in the assignment of the vibrational modes, we obtained the Raman spectra of the yellow and white crystalline forms of dimethyl 3,6-dichloro-2,5-dideuteriooxyterephthalates (partially deuterated yellow and white forms) as well as that of the corresponding quinone:

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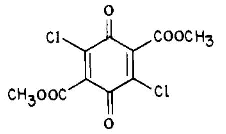
(5) Dwarakanath, K.; Prasad, P. N. *J. Am. Chem. Soc.* **1980**, *102*, 4254.

(6) Misra, T. N.; Prasad, P. N. *Chem. Phys. Lett.* **1982**, *85*, 381.

(7) Prasad, P. N.; Swiatkiewicz, J.; Eisenhardt, G. *Appl. Spectrosc. Rev.* **1982**, *18*, 59.

(8) Swiatkiewicz, J.; Eisenhardt, G.; Prasad, P. N.; Thomas, J. M.; Jones, W.; Theocharis, C. R. *J. Phys. Chem.* **1982**, *86*, 1764.



The vibrational frequencies observed for the corresponding deuterated isomer are displayed in parentheses next to its protovalue; those of the quinone structure are tabulated under a separate column. The mode assignments are also listed in this table. The basis of the assignments of the phonon modes will be discussed in the next section.

An intense band observed at 2964 cm^{-1} for the Y isomer is assigned as the asymmetric deformation of the methyl group. This frequency shows a very small deuteration shift, in agreement with a selective partial deuteration at the 2,5 positions. This vibrational frequency remains basically little affected in the W isomer and in the quinone structure.

From the point of view of hydrogen bonding, the important vibrational frequencies are those associated with the carboxyl group, the phenolic group, and the C–Cl modes. The frequencies of the C=O stretching mode observed for the Y form and the W form are different from each other. The Y form contains a single band at 1682 cm^{-1}, but the W form shows a triplet structure with frequencies of 1718, 1708, and 1698 cm^{-1}. All these frequencies are lower than those observed for the carbonyl groups in the corresponding quinone (1732 cm^{-1}). The quinone structure does not involve any hydrogen bonding. The lowering of the carbonyl frequencies in the Y and W isomers are indicative of the presence of hydrogen bonding.[9] However, the difference in the values (as well as the structures) observed for the Y and W isomers clearly indicates that the nature of the hydrogen bonding is different for the two isomers. The splitting of the C=O stretching mode into a triplet in the W isomer may be owing to a combined effect of the intermolecular hydrogen bonding and the doubling of the unit cell.

The values of the vibrational frequencies observed for the C–OH stretching vibration in both the Y and W isomers are lower than what is usually expected in a non-hydrogen-bonded system. At the same time, the frequency of the O–H in-plane and out-of-plane bonding mode is found to be higher in each isomer. Again, both these observations support the formation of hydrogen bonds.[9]

The nature of this hydrogen bond in the W isomer is further elucidated by an inspection of the C–Cl frequencies. The C–Cl modes, based on the modes of *p*-dichlorobenzene, are expected in the range 290–350 cm^{-1}. The two bands observed for the Y isomer in this frequency range are assigned to the modes associated with the C–Cl group. The bands show a shift toward a lower value, and they split into doublets in the W isomer. The doublet structure may be a result of doubling of the unit cell. In going from the Y isomer to the W isomer, the lowering of the C–Cl mode, specifically that of the β (C–Cl) mode, is in agreement with the presence of a hydrogen-bond interaction, which involves the chlorine atoms in the W isomer. Some of the bands observed in the region 80–250 cm^{-1} have been assigned as the stretching and the deformation modes associated with the hydrogen bond and with the deformation of the C=O and C—OH groups.

The Phonon Modes of the Yellow and White Isomers. The yellow isomer crystallizes in a $P\bar{1}$ space group with one centrosymmetric molecule per unit cell. For this simple lattice structure, only three $k = 0$ librational modes are expected to be Raman active. On the other hand, the unit cell of the white isomer contains twice as many molecules, and six $k = 0$ librational modes are expected to be Raman active. Due to the overlap of the phonon modes with other low-lying modes, the assignment of the phonon modes is complicated. To get some assistance in the assignment of the librational phonon modes, we use the published room-temperature thermal-motion parameters. It has been shown[10,11] that, under favorable conditions, a rigid-body analysis[12] of these thermal-motion parameters can be used to identify the molecular natures of the phonon modes observed in the Raman spectra. As a rigid-motion analysis[12] of the thermal parameters provides an average value of the librational and translational frequencies, such an analysis may be more useful for a simple system such as the Y form, which has one centrosymmetric molecule per unit cell. Also, the intermolecular motions of the Y form should not be affected by the hydrogen bonding, which, in its case, is intramolecular.

Table II. Low-Frequency Modes of the Y and W Isomers at Various Temperatures

isomer	libration principal axis	TMA calculations: (amplitude)^2, (radian)$^2 \times 10^4$	TMA calculations: frequency cm^{-1}	low-frequency modes obsd at various temp: 291 K	95 K	4.2 K
Y	L_2	27.1	34.1	31		
	L_1	78.4	43.1	43.9	47.2	48.0
	L_3	8.6	54.9			
W	L_{1B}[a]	46.7	31.1			49
	L_{2A}	19.9	34.2			51
	L_{2B}	15.4	38.7	47	48.2	52.1
	L_{1A}	43.4	42.9	51.7	55.8	57.7
	L_{3B}	14.9	61.5	57	60.5	62.0
	L_{3A}	13.1	64.0	65	72.5	73.0

[a] The A and B subscripts for the libration axes of the W isomer differentiate two nonequivalent molecules in the unit cell.

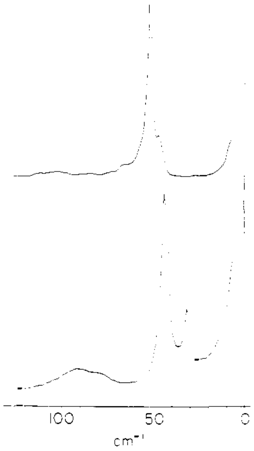


Figure 1. Raman spectra of the polycrystalline W isomer (top) and the Y isomer (bottom) at room temperature. The excitation frequencies are 16 508 cm^{-1} for the Y isomer and 19 433 cm^{-1} for the W isomer.

A thermal-motion analysis (TMA) program was used to calculate the components of the librational (L) and translational (T) tensors with a least-square fit of the published thermal parameters[3] of all non-hydrogen atoms of the molecule. The librational frequencies were calculated by the method of Cruickshank[12] by using the appropriate eigenvalues of the L tensor and the corresponding moments of inertia. The results obtained are listed in Table II. The values for these frequencies are less than 70 cm^{-1}.

Figure 1 shows the Raman spectra, in the frequency range 10–80 cm^{-1}, of the yellow and white isomers at room temperature. In order to minimize orientational effects, we recorded spectra for powdered samples. But for improved resolution, the single-crystal samples at various temperatures were also investigated. The frequencies of the observed modes are listed in Table II. Transitions at 31 and 44 cm^{-1} are observed for the Y isomer at room temperature. These are assigned to correspond to the li-

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(9) Joesten, M. D.; Schaad, L. J. "Hydrogen Bonding"; Marcel Decker: New York, 1974.

(10) Chen., F. P.; Prasad, P. N. *J. Chem. Phys.* **1977**, *66*, 4341.

(11) Bellows, J. C.; Stevens, E. D.; Prasad, P. N. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3256.

(12) Cruickshank, D. W. *Acta Crystallogr.* **1956**, *9*, 1005.

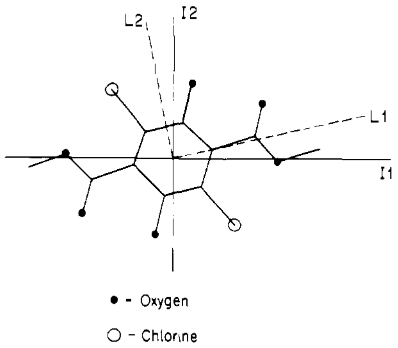

Figure 2. Projection of the Y-isomer molecule and its librational principal axes on the plane defined by the principal axes of the moments of inertia I_1 and I_2.

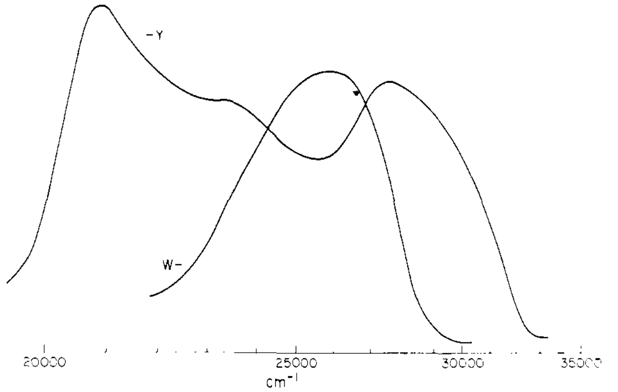

Figure 3. Photoexcitation spectra of the Y isomer and the W isomer, recorded at room temperature.

brations L_2 and L_1, as calculated from the thermal-parameters analysis (Table II). The third mode, related to libration L_3, may be too weak to show up in the Raman spectra. The spectra obtained with the dye laser show a change of the relative intensity of the two phonon modes when the excitation frequency is tuned from 16 000 to 16 850 cm^{-1}. The transition, due to the high-frequency phonon mode, is manifold stronger at the higher frequency excitation. This is taken as an indication of the resonance enhancement of this mode.

In order to investigate the nature of this selective resonance enhancement of the phonon mode, we investigated the details of the librational principal axes with respect to the molecular axes. Figure 2 shows a projection of the molecule (Y isomer) on the plane defined by the principal axes for moments of inertia I_1 and I_2. The L_3 axis practically coincides with the I_3 axis, and the L_1 axis is directed nearly along the long axis of the molecule. The L_1 libration has the highest amplitude (~5°), and, possibly, it heavily interferes with the twisting vibration of the COOMe groups. Therefore, it can modulate the lowest electronic transition, which is of $n \rightarrow \pi^*$ type. This effect can give rise to a selective resonance enhancement of the intensity for the L_1 librational mode. The calculated L_1 librational frequency matches with that observed for the most intense resonance-enhanced mode in the phonon spectrum.

The results of a similar analysis for the W isomer are, however, less conclusive. The spectra recorded, both for the powdered samples and the single crystals at room temperature, are poorly resolved. The resolution is found to improve considerably at 95 K, and even more so at 4.2 K (see Table II). The assignments based on the rigid-body analysis of the thermal parameters of the white isomer is complicated because the librational axes do no relate to the molecular axes in a simple manner. Furthermore, there is a mismatch between the librational axes and the ones for the corresponding moments of inertia. Such a mismatch would be expected from the presence of hydrogen bonding in the W form. These complications may account for the discrepancies between the calculated and observed frequencies for the W isomer (Table II).

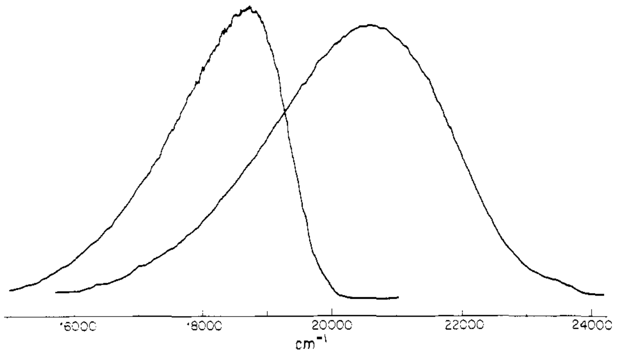

Figure 4. Emission spectra of the Y isomer (left) and the W isomer (right), recorded at room temperature.

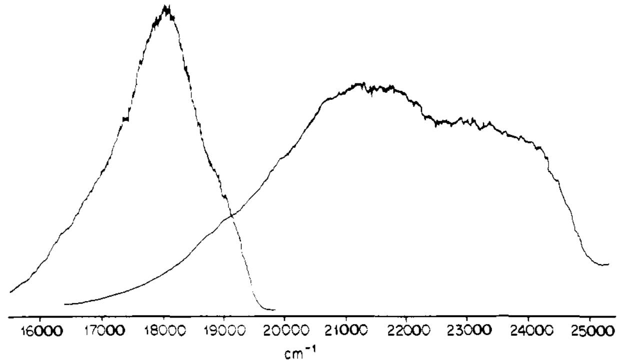

Figure 5. Emission spectra of the Y isomer (left) and the W isomer (right), recorded at 30 K.

Electronic Photoexcitation and Emission Studies. The photoexcitation and emission spectra of the Y isomer and the W isomer, recorded at room temperature, are shown in Figures 3 and 4, respectively. The bands are structureless. There is approximately 55 nm of Stokes shift between the maxima of the photoexcitation and the emission spectra for the Y form. The Stokes shift for the W form is 97 nm.

The emission spectra of both isomers, recorded at 30 K, are shown in Figure 5. The bands are still broad, which suggests a strong vibronic coupling as is often observed for the hydrogen-bonded systems. The emission band of the Y isomer at 30 K is narrower than that observed at room temperature and is shifted toward lower energy. At 30 K, the emission spectrum of the W isomer consists of two relatively broad bands, whereas the emission spectrum recorded at room temperature consists of only one lower energy band. This result may be a consequence of an efficient energy transfer, at room temperature, from the high-energy state to the low-energy state. A preliminary study reveals that the low-energy emission is long-lived. A complete understanding of this temperature behavior will require a more detailed spectroscopic study of the electronic states. The present paper does not focus on this aspect.

At high temperatures (such as 390 K), where the rearrangement occurs readily, the samples show emissions that are shifted in their maxima from the room-temperature value and show broadening. Therefore, these electronic spectra can be used to characterize the Y and W isomers for studying the rearrangement.

The emission maximum of the W isomer is close in energy to the maximum of the photoexcitation profile of the Y isomer. Hence, the emission from the W isomer, in the partly converted Y isomer sample, may be absorbed by the surrounding Y isomer, which leads to emission only from the Y isomer. Also, a direct energy transfer from the W form to the Y form may take place if the two isomers form a solid solution. Although the photoexcitation spectra at room temperature are different for the Y isomer and the W isomer, the maximum for the W form is situated between the overlapping broad bands of the Y form. The emission

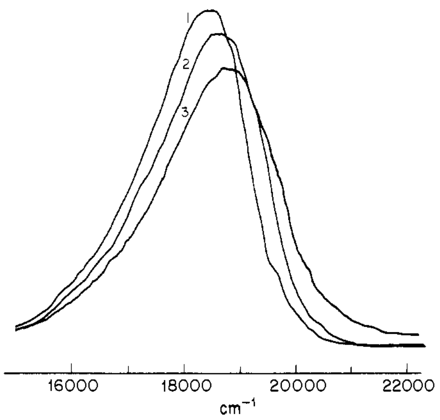

Figure 6. Emission spectra of the Y-isomer single crystal, monitored as a function of time, after raising the temperature of the crystal to 383 K. The spectra 1, 2, and 3 were obtained after 5, 100, and 175 min, respectively.

spectra of the two forms at room temperature or above have distinctly separated maxima. Consequently, they can more conveniently be used to characterize these isomers.

Mechanism of the Solid-State Rearrangement. Because the crystals of the Y isomer, fortunately, emit at the conversion temperature, both the electronic emission spectra and the Raman phonon spectra were used in conjunction to investigate the reaction mechanism. At this point, it may perhaps be appropriate to discuss the relative merits of these two spectroscopic techniques. Raman spectroscopy is applicable to all solid-state reactions and, therefore, is more general. Electronic emission spectroscopy is applicable only to emissive samples. Unfortunately, Raman spectroscopy is limited in its sensitivity and is very useful in probing the conversion of $\geq 1\%$. Emission spectroscopy is highly sensitive and more suitable for the very initial stage of the reaction. The limitations of emission spectroscopy are the lack of detailed information regarding the chemical nature of the rearrangement, its dependence on the crystal quality, and the complication due to energy transfer. Therefore, a combination of these two techniques can be more informative when the reactant or the product or both emit under the reaction condition. Emission spectroscopy can provide valuable information regarding the mechanism of the process at the initial state ($<1\%$) where the Raman method is not sensitive. After the initial stage and throughout the conversion range ($\geq 1\%$), Raman spectroscopy is the preferred technique for the investigation of the reaction.

In order to study the early stage of the rearrangement, we recorded the emission spectra as a function of time at 383 K. On the basis of our observation, the experiment time can be divided into three distinct stages. During the first stage, which spanned to 100 min of heating at 383 K, the single crystal of the Y isomer remained intact, but the emission maximum shifted monotonically to a higher frequency by about 250 cm^{-1}. This shift in the emission maximum is also accompanied by the broadening of the spectra profile. These features can readily be seen in Figure 6, which exhibits two emission spectra recorded after 15 and 100 min at 383 K. During the second stage, i.e., after 100 min, the single crystal of the Y isomer cracked into small crystallites. The emission spectrum recorded after 175 min at 383 K is also shown in Figure 6. The emission maximum has shifted by another 200 cm^{-1}; there is also further broadening. The third stage starts somewhere around 175 min. After this time, there is essentially no change in the position of the emission maximum but only some further broadening of the spectral profile. A visual inspection showed that the crystal remained yellow even after 4 h at 383 K. The Raman phonon spectra of this sample indicated the formation of a small amount of the W isomer as a separate phase.

The results of the above emission studies can be interpreted as follows. The first stage is the initial phase of rearrangement. During this stage, the observed shift in the emission maximum is similar in magnitude to what is observed under an applied uniform external pressure.[13] A uniform pressure creates a homogeneous strain on the unit cell level. We, therefore, conclude that the rearrangement process, in the initial phase, creates a homogeneous internal strain field, which gives rise to the shift of the emission maximum and a broadening of the spectral profile. This homomogeneous internal strain may arise either from the formation of the W isomer randomly distributed as a solid solution in the Y isomer lattice or from an intermediate structure that converts to the W isomer later. As the rearrangement, at this stage, is too small to be probed by Raman spectroscopy, we cannot conclusively establish the exact nature of the initial process. In either case, the results of the study indicate that the rearrangement, at this initial stage, involves a homogeneous mechanism. The distortion of the reactant lattice, created by further rearrangement, is severe enough to break the lattice and crack the crystal. However, despite the crystal fracture, the emission spectra show that the strain created within the reactant lattice still exists. Perhaps, a small phase separation of the W isomer product may already occur at this stage of the rearrangement. The process of phase separation of the W isomer is evident when the Raman phonon spectroscopy becomes adequately sensitive to the conversion. The thermal rearrangement process now involves a heterogeneous mechanism.

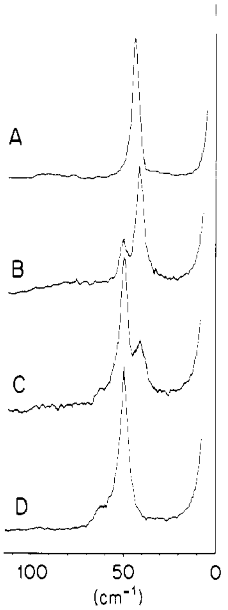

Figure 7. Raman phonon spectra recorded as a function of the advancement of the rearrangement: (A) the spectrum of the Y-isomer single crystal at 291 K; (B) an intermediate stage of the rearrangement, the spectrum recorded at 363 K after about 1 h of annealing at this temperature; (C) an intermediate stage of the rearrangement after annealing at 378 K; (D) the W-isomer polycrystalline sample, the spectrum recorded after complete rearrangement at 397 K.

A detailed investigation of the rearrangement above 1% of conversion (estimated value) was performed by low-frequency laser Raman spectroscopy. The Raman phonon spectra of a single crystal of the Y form were recorded at elevated temperatures. Figure 7 shows the Raman phonon spectra obtained as a function of the reaction progress. The phonon spectra at the intermediate conversion can be explained as a superposition of the unperturbed phonon bands of the Y and W isomers. As the conversion increases, the phonon bands of the W isomer gain intensity relative to the bands of the Y isomer. This result shows that no solid solution is formed[5,8] between the Y isomer and the W isomer. This is found to be the case for the entire conversion range sensitive to the Raman phonon spectra (concentrations $\geq 1\%$). This observation indicates a heterogeneous mechanism.

The behavior shown by the rearrangement of dimethyl 2,6-dichloro-2,5-dihydroxyterephthalate is similar to that shown by

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(13) Nicol, M. F.; Hara, Y.; Wiget, J. M.; Anton, M. *J. Mol. Struct.* **1978**, *47*, 371.

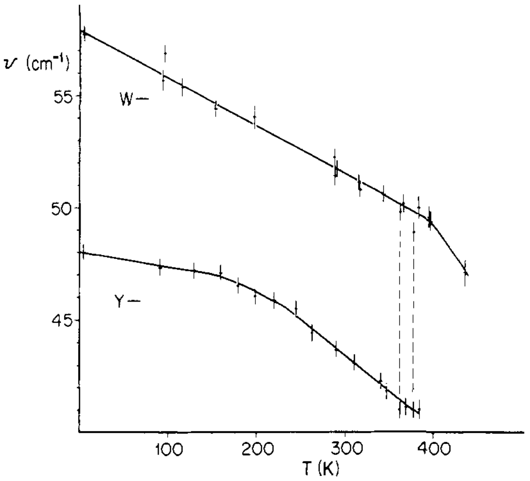

Figure 8. Frequency of the strongest libration mode of the Y isomer (L_1 libration) and of the W isomer as a function of temperature. The vertical lines join the points related to the peaks observed in the spectra presented in Figure 7, B and C.

the photodimerization of 2,6-dimethylbenzoquinone in the solid state.[6] The only difference is that, in the case of 2,6-dimethylbenzoquinone, the reaction is homogeneous to the extent of conversion when it can manifest itself in the Raman phonon spectra. Then, with further accumulation of the product, the photodimerization process becomes heterogeneous. Therefore, both the initial homogeneous stage and the later heterogeneous stage of the photodimerization of 2,6-dimethylbenzoquinone were successfully probed by Raman phonon spectroscopy. In contrast, the thermal rearrangement of the Y isomer in the solid state is homogeneous only at the very initial stage, which is not detectable by the sensitivity limit of Raman phonon spectroscopy.

In order to investigate the possibility of a phonon mode-softening,[5,7] which could assist the rearrangement process, we monitored the phonon spectra of the crystal of the Y isomer as a function of temperature. The results are displayed in Figure 8. The most prominent band, the libration L_1 in the Y isomer, shows a monotonic lowering of frequency. But no over-damped behavior is observed for this mode as the sample temperature approaches the point where rearrangement takes place. From the nature of the rearrangement, which can be explained by invoking a near 180° rotation of the molecule, the corresponding libration, L_2, in the Y isomer can also assist the rearrangement, if this mode softens. Unfortunately, the Raman transition for the L_2 libration is weak and gets buried under the transition for the L_1 libration, as the bands broaden at a higher temperature. Hence, our study cannot provide any conclusion regarding the possiblity of softening of the L_2 mode.

The kinetics of the transformation of the Y isomer in a single crystal occurs over a very wide range of temperature. Some samples are resistant to rearrangement even up to 390 K. These samples were used for the temperature-dependence study of the frequency of the L_1 mode. Other samples transform at a much lower temperature (363 K). It is the latter-type sample that was used for the study represented in Figure 6.

As the rearrangement rate appears to be highly dependent on the crystal history, it may be assumed that the rearrangement process is defect controlled. It should be noted that the α–β phase transition in the single crystal of *p*-dichlorobenzene also involves a significant molecular reorientation.[14] This phase transition has been shown to be defect controlled,[15] and it does not involve any phonon mode-softening.

The temperature-dependence study of the internal modes shows no anomaly for the Y isomer crystal. Contrary to this, a similar study of the W isomer crystal reveals that the modes associated with hydrogen bonding in this crystal show a rapid decrease in intensity as the temperature is raised. Also, when the Y isomer crystal is converted to the W isomer (polycrystalline sample) at high temperature, the modes associated with the hydrogen bond in the W isomer do not show up immediately. Once the crystal is cooled and left for sometime, these modes appear. This observation suggests that, in the conversion of the Y isomer to the W isomer, the development of the intermolecular hydrogen bond is probably the last process involved in the rearrangement mechanism.

Conclusions

The Y and the W isomers of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate in the solid state have been characterized by using Raman spectra to be different in the nature of the hydrogen bonds. The rigid-motion analysis of the thermal parameters was used in conjunction with the Raman phonon spectra to make assignments of the phonon bands. Because of the emissivity of the Y form at the rearrangement temperature, electronic emission spectroscopy was combined with Raman phonon spectroscopy to determine the reaction mechanism. It was found that the rearrangement starts initially as a homogeneous process and becomes heterogeneous when only a small amount of the W isomer forms. The temperature-dependence study of the phonon spectra did not reveal any phonon mode-softening, which suggests that the rearrangement may be defect controlled and not phonon assisted. The present work also provides some insight into a molecular understanding of this rearrangement process. It shows that, in the conversion of the Y isomer to the W isomer, the development of the hydrogen bond, which is characteristic of the product, lags behind the structural rearrangement of the Y isomer. While the present result does not elucidate the nature of the molecular reorientation, it suggests that the reorientation is not a phonon-assisted process.

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Registry No. 2,5-Dicarbomethoxy-1,4-cyclohexanedione, 6289-46-9; dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate, 24648-18-8; 3,6-dichloro-2,5-dicarbomethoxybenzoquinone, 25186-39-4; dimethyl 3,6-dichloro-2,5-dihydroxy-2,5-dideuterioterephthalate, 83605-41-8.

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(14) Crafts, D. L.; Bellows, J. C.; Prasad, P. N. *J. Raman Spectrosc.* **1978**, *7*, 316.

(15) Reynolds, P. A. *Acta Crystallogr., Sect. A* **1977**, *A33*, 185 and references therein.