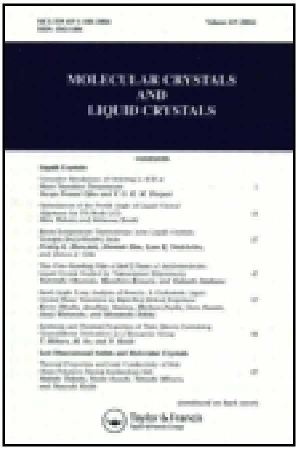


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Laser Raman Investigation of Solid State Rearrangement of bis(O-Iodobenzoyl) peroxide into 1-(2'-Iodobenzoyloxy)-1, 2-benziodoxolin-3-one

Kaddi Dwarakanath [a] [b] , R. Burzynski [a] & Paras N. Prasad [a]

[a] Department of Chemistry, State University of New York at Buffalo, Buffalo, NY, 14214

[b] Chemistry Department, Illinois Institute of Technology, Chicago, Illinois, 60616

Version of record first published: 20 Apr 2011.

To cite this article: Kaddi Dwarakanath , R. Burzynski & Paras N. Prasad (1983): Laser Raman Investigation of Solid State Rearrangement of bis(O-Iodobenzoyl) peroxide into 1-(2'-Iodobenzoyloxy)-1, 2-benziodoxolin-3-one, Molecular Crystals and Liquid Crystals, 100:1-2, 31-40

To link to this article: http://dx.doi.org/10.1080/00268948308073716

Mol. Cryst. Liq. Cryst., 1983, Vol. 100, pp. 31–40
0026-8941/83/1002-0031/$18.50/0

Printed in the United States of America

Laser Raman Investigation of Solid State Rearrangement of bis(*O*-Iodobenzoyl) peroxide into 1-(2′-Iodobenzoyloxy)-1, 2-benziodoxolin-3-one †

KADDI DWARAKANATH‡, R. BURZYNSKI§ and PARAS N. PRASAD ||

Department of Chemistry, State University of New York at Buffalo,
Buffalo, NY 14214

(*Received March 16, 1983*)

In solid state, the thermal rearrangement of bis(*O*-iodobenzoyl) peroxide which yields 1-(2′-iodobenzoyloxy)-1,2-benziodoxolin-3-one, is investigated by laser Raman spectroscopy. The intramolecular vibration spectra are used to characterize this chemical rearrangement. The phonon spectra obtained as a function of the rearrangement progress show that, in spite of the reported topotactic nature of the reaction, it proceeds by a heterogeneous mechanism. A temperature dependence study of the phonon spectra reveal no mode-softening for any optical phonons. Therefore, no evidence has been found for this reaction to be phonon-assisted.

INTRODUCTION

The area of solid state reactions has received a renewed interest during the recent years and it is a highly active field of research.[1-3] The reason for this increased attention has been the recognition that solid

---

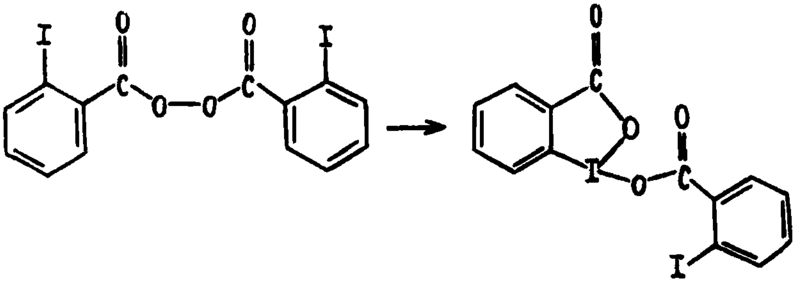
†Supported in part by NIH grant # 1R01GM2735703 and in part by AFOSR grant # 800287.

‡Present address: Chemistry Department, Illinois Institute of Technology, Chicago, Illinois 60616.

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

|| To whom all correspondence should be addressed.

state reactions are highly selective and can produce monomeric and polymeric materials which are not obtainable from solution chemistry. An exciting prospect, in this regard, is chiral synthesis by solid state reactions.[1] This paper reports a study of the thermal rearrangement of bis(*O*-iodobenzoyl) peroxide (Structure I shown below) which in solid state yields 1-(2′-iodobenzoyloxy)-1,2-benziodoxolin-3-one (Structure II shown below).[4-7]



I II (1)

This reaction has been suggested to take place by a free radical mechanism[4,5] involving the rupture of the peroxide bond. At room temperature, it takes several weeks to achieve a quantitative transformation of I into the product II. The reaction can be greatly accelerated by heating the reactant crystal. For example, the quantitative conversion takes place in only several hours if the reactant is heated to 55 °C. The same rearrangement also takes place in several solutions.[4] This specific thermal rearrangement, in solid state, exhibits a number of interesting features:[5-7] (i) The reaction has been classified as topotactic, because it yields a crystal of the product in which the molecules assume preferred orientations relative to crystallographic directions of the reactant structure. (ii) The product has been found to exist in two polymorphic crystalline forms α and β, but the rearrangement below the $\alpha \rightarrow \beta$ transformation temperature (110 °C) has been suggested to produce only the α-modification of the product.[6] (iii) Although, the rearrangement reaction is intramolecular, the formation of the product lattice from the reactant lattice also involves a significant molecular reorientation.[5,6] (iv) The oriented product produced by this rearrangement may be degraded further by two different, competing and consecutive reactions to produce *O*-iodosobenzoic acid and *O*-iodobenzoic acid.

The solid state rearrangement represented by Eq. 1 is investigated by the laser Raman spectroscopy. The laser Raman spectroscopy is a highly suitable technique for the investigation of solid state reactions.[8]

First, it can be conveniently used to finger-print the product and identify the molecular nature of the reaction. Second, the method of Raman phonon spectroscopy, introduced recently by this research group,[8-11] is highly suitable for the determination of the reaction mechanism from the point of view of the mode of formation of the product. The two possible mechanisms for the formation of the product are:[2] (i) A homogeneous mechanism which involves a single phase comprised of the solid solution of the reactant and the product, (ii) a heterogeneous mechanism in which the reactant and the product segregate in two distinct phases. The phonon bands (intermolecular lattice modes) are highly sensitive to local interactions and, therefore, can readily determine if a reaction is truly homogeneous at the molecular level. Third, the Raman phonon spectra can also be used to derive information on the role of the phonon motions in determining a thermal reaction. In this context, a novel concept of phonon-assisted reactions has been recently introduced.[8-11] A thermal reaction can be phonon-assisted by the softening of a specific phonon mode which creates large amplitude displacements along the reaction coordinate.[9] Although, the reaction coordinate, in the case of rearrangement of bis(*O*-iodobenzoyl) peroxide, is intramolecular, the formation of the product lattice, as discussed above, does involve molecular reorientation in the lattice. In view of this fact, there is a possibility that the required molecular reorientation may be phonon-assisted.

These aspects of solid state reactions are investigated for the rearrangement reaction of bis(*O*-iodobenzoyl) peroxide. Raman spectra are obtained for the reactant and the product both in the phonon and the internal vibration region. The entire conversion range is monitored by following the spectral changes during the rearrangement. For the investigation of the possibility of a phonon mode softening, the Raman phonon spectra are studied as a function of temperature.

EXPERIMENTAL

The material bis(*O*-iodobenzoyl) peroxide (compound I) was prepared and characterized according to the method described by Leffler *et al.*[4] The product II, 1-(2′-iodobenzoyloxy)-1,2-benziodoxolin-3-one, was obtained by two methods: (a) by heating compound I at ~ 55 °C for several hours,[5] and (b) by allowing the rearrangement of I in a benzene solution (which takes place in a period of 12 hours).

The reactant I is not stable when dissolved in most solvents. This posed some problems in growing large single crystals. The large crystals obtained from a solution in dichloromethane was found to be of *O*-iodobenzoic acid instead of I or II, indicating a different type reaction in dichloromethane. The mechanism for the reaction of I in the solution has been discussed by Honsberg and Leffler.[12] The small crystals of I were obtained from a mixture of dichloromethane and methanol at −30 °C. A polycrystalline sample was used to obtain the Raman spectra. The Raman spectra were recorded on a Spex model 14018 double monochromator by using the 5145 Å line from an argon ion laser (coherent model CR-8) as the excitation source. For spectroscopic studies at low temperatures, the sample was cooled by a flow of cold nitrogen vapor. To obtain spectra at elevated temperatures, a flow of warm nitrogen gas was used in the same arrangement. The temperature was measured by a chromel-constantan thermocouple. The spectra were recorded in a dc detection mode.

RESULTS AND DISCUSSIONS

1. Characterization of the reactant and the product

For this purpose, the Raman spectra of the reactant and the product were obtained. The observed vibrational frequencies in the Raman spectra are listed in Table I. The space group of the reactant I is Pc with two molecules per unit cell. Therefore, 9 Raman active phonon modes are expected. In molecular crystals, the phonon modes are found to be generally less than 200 cm^{-1} in frequency. In the case of the reactant (I), we observed 10 transitions below 200 cm^{-1}. These transitions are tentatively assigned as phonon modes. It may be that some of these are low-lying internal modes, but for the purpose of this work, such possibilities do not bring any complications. In the case of the product, two polymorphic phases have been found. We have characterized these two forms of the product by their phonon spectra as shown in Figure 1. We find that the product of our solid state rearrangement study is the α-modification. Considering that the rearrangement reaction was conducted below the $\alpha \rightarrow \beta$ transformation temperature (110 °C), only α-modification of the product is expected to form. The α-form crystallizes in a space group Cc, $Z = 8$. For this structure, the site symmetry, again, is C_1, and there are four molecules per Bravais cell. Therefore, 21 phonon transitions can be expected in Raman spectra. Experimentally, sixteen distinguishable transitions are observed below 200 cm^{-1}. The β-phase of II crystallizes in space group $P2_1/c$, $Z = 4$. For this space group, 12 Raman-active phonon modes are expected. We observe fifteen transitions within the spectral

TABLE 1

Observed vibrational frequencies (cm^{-1}) of the reactant and the product in the Raman spectra

Reactant	Product	Reactant	Product
25.0 (w)	17.5 (m)	889.5 (m-s)	448.0 (m)
32.0 (w)		998.0 (w)	454.0 (m)
37.0 (mw)	24.0 (m-s)	1008.0 (w)	670.5 (vs)
42.5 (vs)	28.5 (w)	1011.0 (w)	575.0 (s)
59.5 (w)	32.5 (w)	1026.0 (s)	660.0 (m-s)
69.5 (m)	37.5 (s)	1030.0 (s)	651.5 (m-s)
109.0 (vw)	47.0 (vs)	1034.0 (s)	695.0 (s)
130.0 (w, sh)	51.0 (s)	1059.5 (m)	699.0 (m)
159.0 (vw)	55.5 (s)	1165.0 (m)	822.0 (m)
193.5 (w)		1175.0 (m)	825.0 (m)
214.0 (vw)	69.0 (s)	1220.0 (m)	858.0 (m-s, sh)
222.0 (vw)	79.5 (w, sh)	1290.0 (w)	862.0 (s)
251.0 (vs)	86.0 (m, sh)	1563.0 (w)	1008.0 (w)
290.0 (w)	121.0 (mw)	1579.0 (s)	1018.0 (w-m, sh)
314.0 (w)	138.0 (mw)	1776.0 (m-w)	1027.0 (s)
331.0 (w)	141.5 (mw)	1794.0 (m-w)	1037.0 (m)
367.0 (vw)	150.5 (w)		1118.0 (w)
392.0 (w-m)	181.0 (w)		1139.5 (m-s)
402.5 (w)	210.0 (w)		1163.5 (s)
408.5 (w, sh)	218.0 (w)		1245.0 (m-w)
497.0 (w)	230.0 (w)		1322.0 (w)
498 (w)	238.0 (m)		1578.0 (sh, m)
639.5 (s)	247.0 (ms)		1586.0 (s)
673 (w-m)	258.0 (s)		1629.5 (m-s)
679 (w)	285.0 (s)		1685 (m, sh)
848 (m)	292.0 (s)		1700 (m-s)
879 (m)	322.0 (vs)		1709 (m-s)

range 0–200 cm^{-1}. We assign the increased number of bands due to low-lying internal modes.

In the internal vibration region (> 200 cm^{-1}), the spectra of the reactant and the product show significant differences, typifying a chemical reaction rather than a physical (phase) transformation. The bands observed at 1776 and 1794 cm^{-1}, in the Raman spectra of I, are assigned as the acid peroxide modes. These bands completely disappear during the rearrangement. This result is consistent with the rearrangement reaction producing II from I, which involves a rupture of the peroxide bond. New bands appear in the spectra of the product. The most prominent and characteristic bands of the product are at 575 cm^{-1}, 1629.5 cm^{-1} and 1685, 1700 and 1709 cm^{-1}. The IR spectra of the crystal IIα have been reported[6] for the region of the carbonyl frequencies (1600 cm^{-1}–1700 cm^{-1}). In this region, the α-phase (which has been reported to be the product if the rearrangement occurs below 110 °C) shows two equally intense peaks at 1700 and 1629.5 cm^{-1}. Therefore, our observation of prominent features around

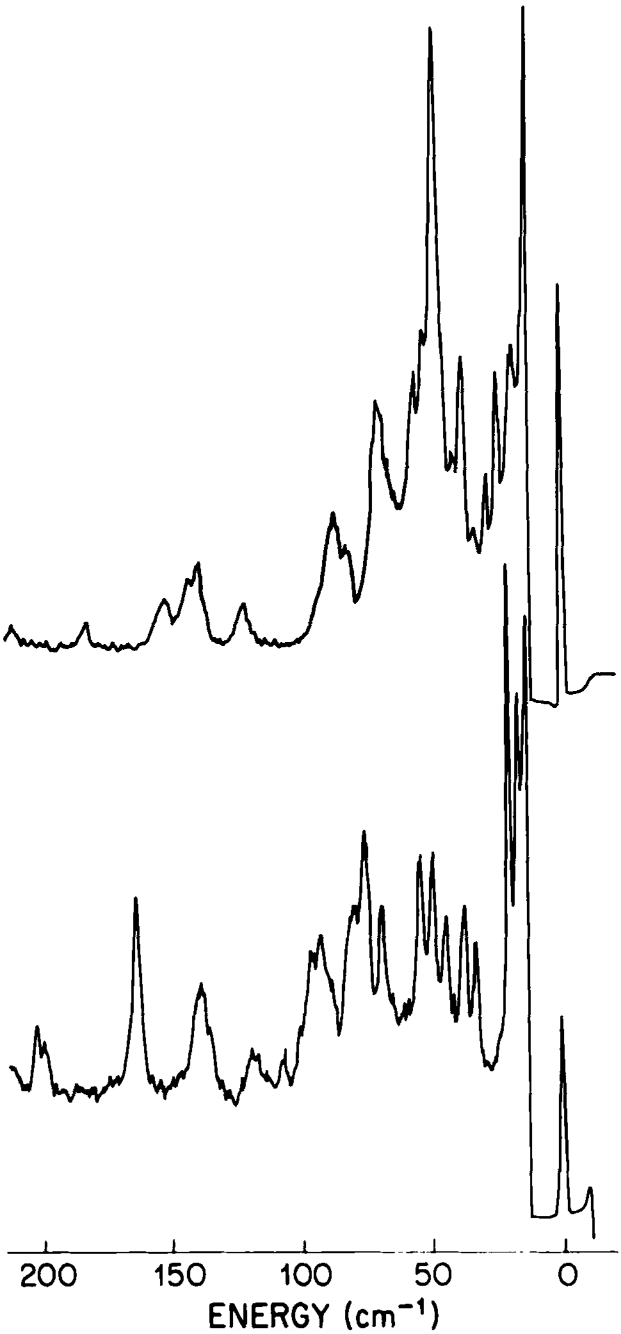


FIGURE 1 Raman phonon spectra of the two polymorphic forms of the product, at 120 K are compared. The top spectrum is of the α-form; the bottom spectrum belongs to the β-form.

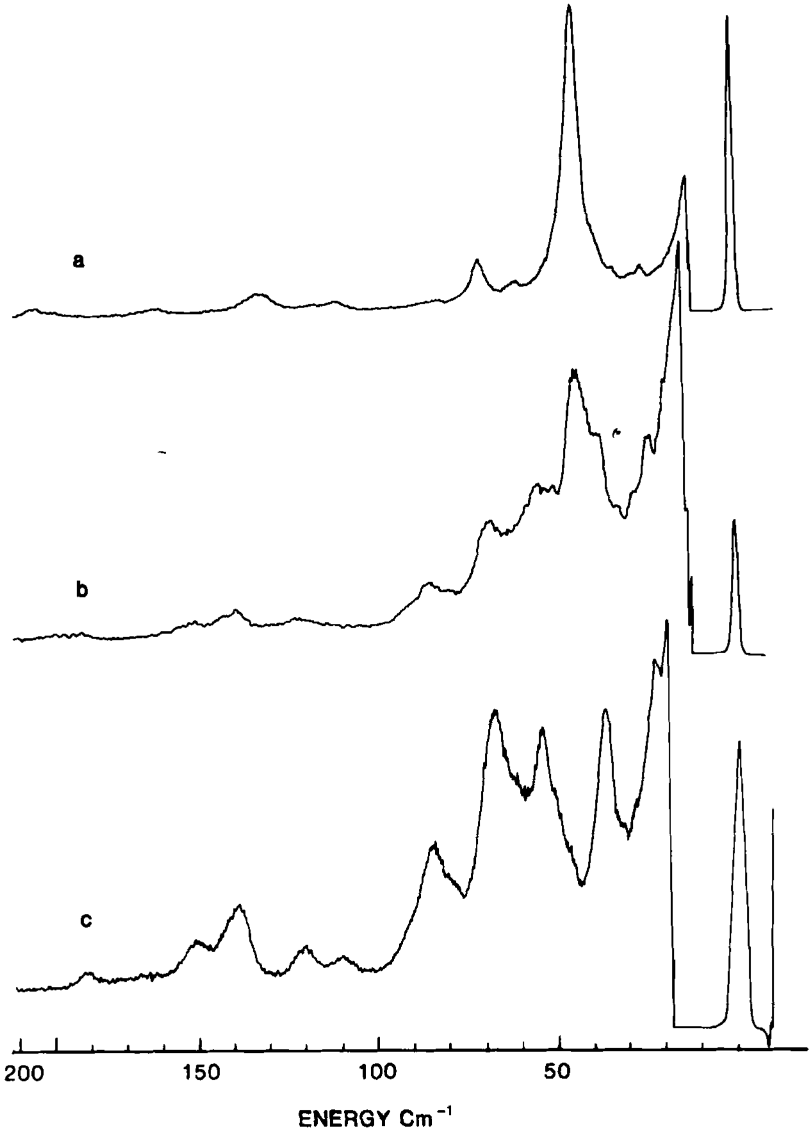


FIGURE 2 Raman phonon spectra of the reactant (a), an intermediate conversion sample (b), and the rearrangement product (c). These spectra were recorded with the samples at 120 K. The spectral resolution is ~ 1 cm^{-1}.

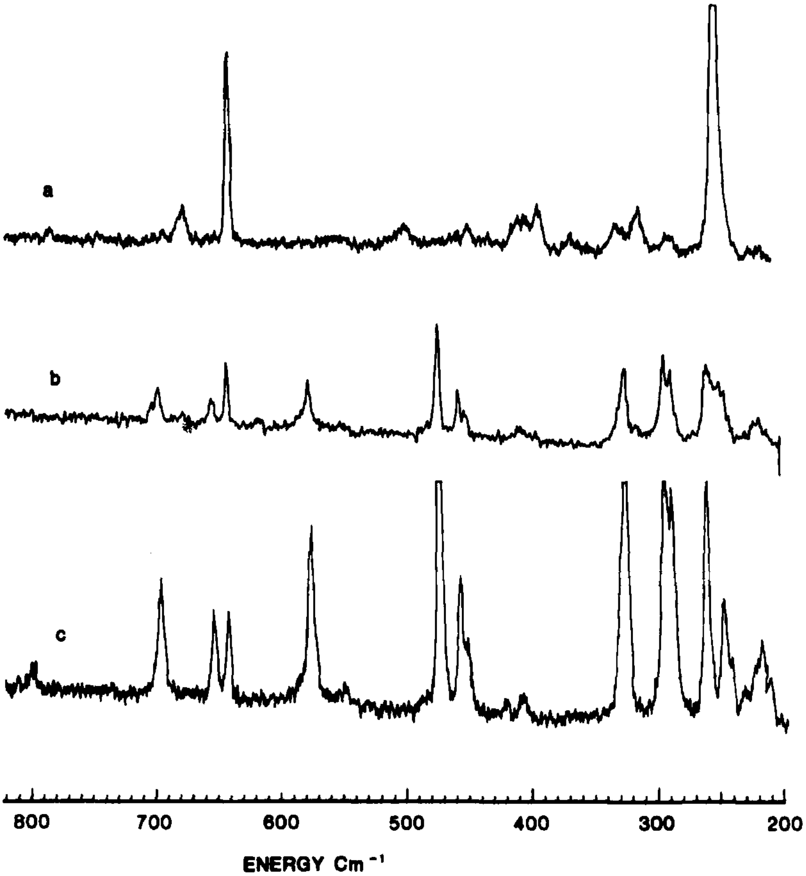


FIGURE 3 Raman spectra, in the vibrational region 200 cm^{-1} to 800 cm^{-1}, of the reactant (a), an intermediate conversion sample (b), and the rearranged product (c), all at 120 K. The spectral resolution is ~ 1 cm^{-1}.

1700 cm^{-1} in the Raman spectra of the product is in agreement with the IR spectra of II which is noncentrosymmetric.

2. Mechanism of the rearrangement

Both the phonon spectra and the spectra of some low-lying intramolecular vibrations were monitored as a function of the rearrangement progress. Figure 2 shows the phonon spectra monitored during the rearrangement. It can be seen that, as the rearrangement progresses, the phonon bands of the product appear to gain intensity while those of the reactant decrease in intensity. During the intermediate conversion range, the observed phonon spectra are simple superposition of

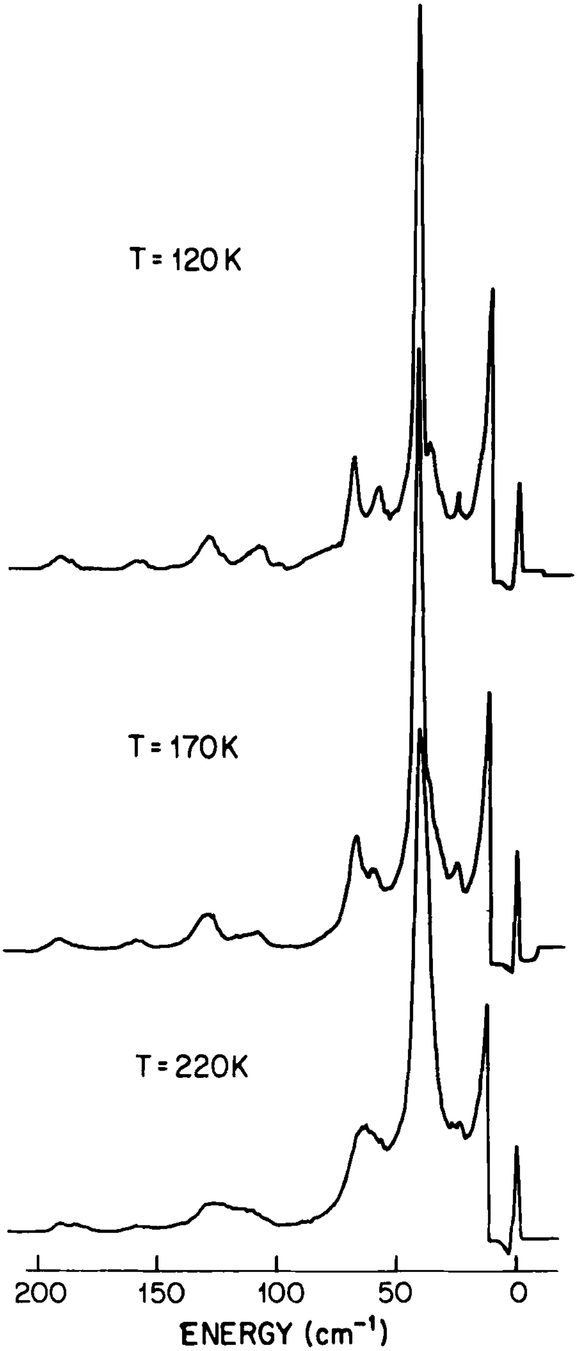


FIGURE 4 The phonon spectra of the reactant at three different temperatures are displayed.

the unperturbed phonon bands (in frequency) of the reactant and the product. Figure 3 shows the low-lying intramolecular bands as a function of the rearrangement progress. Again, the same type of behavior is observed. The observed spectral features, during the intermediate conversion, are found to be a superposition of the bands of the reactant and the product. These observations point out a heterogeneous mechanism for the thermal rearrangement of I. This result is interesting in view of the fact that the reaction has been noted to be topotactic, that is, it produces product lattice in orientations related to that of the reactant lattice. This behavior is similar to what is observed for the $\alpha \rightarrow \beta$ phase transition of *p*-dichlorobenzene which also produces well-oriented β phase from the α-phase, but is otherwise, distinctly, a two-phase process.

To investigate the possibility of phonon-mode softening, which may assist the rearrangement, a temperature dependence study of the phonon spectra was conducted. The phonon spectra of the reactant at three different temperatures are displayed in Figure 4. Except for a small shift in the peak positions and a spectral broadening, no evidence for a phonon-mode softening was observed. From this result, it may be assumed that the process is not phonon-assisted. In view of the fact that the rearrangement reaction is primarily intramolecular, it is not surprising that the process is not phonon-assisted.

References

1. D. Y. Curtin and I. C. Paul, *Chem. Rev.*, **81**, 525 (1981) and references therein.
2. J. M. Thomas, S. E. Morsi, and J. P. Desvergne in "Advances in Physical Organic Chemistry", Vol. 15, ed. by V. Gold and D. Bethell, Academic Press, Inc. (London, 1977, p. 63).
3. G. Wegner, *Pure Appl. Chem.*, **49**, 443 (1977).
4. J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5435 (1958).
5. J. Z. Gougoutas, *Pure Appl. Chem.*, **27**, 305 (1971); *Israel J. Chem.*, **10**, 395 (1972).
6. J. Z. Gougoutas and J. C. Clardy, *J. Solid State Chem.*, **4**, 230 (1972).
7. J. Z. Gougoutas, *J. Am. Chem. Soc.*, **99**, 127 (1977).
8. P. N. Prasad, J. Swiatkiewicz and G. Eisenhardt, *Appl. Spectroscopy Rev.*, **18**, 59 (1982).
9. K. Dwarakanath and P. N. Prasad, *J. Am. Chem. Soc.*, **102**, 4254 (1980).
10. T. N. Misra and P. N. Prasad, *Chem. Phys. Lett.*, **85**, 381 (1982).
11. J. Swiatkiewicz, G. Eisenhardt, P. N. Prasad, J. M. Thomas, W. Jones and C. R. Theocharis, *J. Phys. Chem.*, **86**, 1764 (1982).
12. W. Honsberg and J. E. Leffler, *J. Org. Chem.*, **26**, 733 (1961).
13. W. G. Fateley, F. R. Dollish, N. T. McDevitt and F. F. Bentley, "Infrared and Raman Selection Rules for Molecular and Lattice Vibrations," John Wiley (New York, 1972).