

# Molecular Structure of 5,5'-Bis-Isoxazole

## Part I.—Vibrational Assignment and Dipole Measurement

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Infra-red and Raman spectra of 5,5'-bis-isoxazole- $\text{h}_4$  and - $\text{d}_4$  in the crystal state and in solution have been measured and the dichroism of the infra-red bands in polycrystalline samples has been determined. The data obtained are consistent with a trans planar structure in the crystal. In the liquid state and in solution, the molecule exists in a single distorted configuration, as shown by the spectra at different temperature and by the value of the dipole moment. An almost complete assignment of the fundamentals in the crystal has been obtained.

Molecules like biphenyl and bipyridyl, containing two rings connected by a central C—C bond, exist in a different conformation depending upon the state of aggregation. They are constrained into a planar structure by the intermolecular forces in the crystal, whereas they assume more loose non-planar configurations in the liquid and gas phases, as shown by X-rays,<sup>1, 2</sup> electron diffraction,<sup>3, 4</sup> n.m.r.,<sup>5, 6</sup> i.-r.,<sup>7, 8</sup> and u.-v.<sup>9</sup> spectroscopy.

5,5'-bis-isoxazole is another two rings compound (fig. 1) which is expected, in principle, to have a similar behaviour.

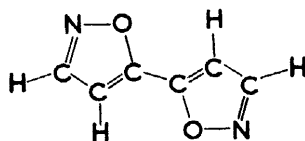


FIG. 1.—5,5'-bis-isoxazole.

Like bipyridyl, it also has the possibility of cis and trans planar isomers. The only available data are an X-ray investigation,<sup>10</sup> which has proved that the molecule is trans planar in the solid state.

In order to investigate the molecular structure in the liquid phase, we undertook a detailed analysis of its vibrational spectrum. Because of the great complexity of the spectrum, it was necessary, before interpreting that of the liquid, to obtain a clear understanding of the much simpler crystal spectrum. This was obtained through the analysis of the Raman spectrum and of the i.-r. spectrum in polarized light of oriented crystalline samples of both bis-isoxazole and its fully deuterated homologue. The liquid spectrum, showing new bands due to a distorted configuration, was interpreted

with the aid of the assignment for the crystal. Additional data on the molecular conformation in solution were obtained from the dipole moment.

### EXPERIMENTAL

5,5'-bis-isoxazole- $\text{h}_4$  and - $\text{d}_4$  were prepared according to methods already reported.<sup>11, 12</sup> Both isotopes were purified by several crystallizations from  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  and sublimations.

Infra-red spectra in polarized light were measured on polycrystalline oriented films grown between two KBr plates, with the aid of a Beckman IR-9 spectrometer in the  $4000\text{--}400\text{ cm}^{-1}$  range. Infra-red spectra of 5,5'-bis-isoxazole- $\text{h}_4$  at liquid nitrogen temperature were also obtained on oriented samples, using a low-temperature conventional cell and a Perkin-Elmer 225 double-grating instrument, between  $4000$  and  $200\text{ cm}^{-1}$ .

The spectra of the liquid were measured by melting the sample between two KBr windows and maintaining it at  $120^\circ\text{C}$  in a variable temperature cell. A 1-mm-thick sealed cell was then employed to obtain spectra of solutions at different temperatures using  $\text{CHCl}_3$  (from  $-40$  to  $+30^\circ\text{C}$ ) and nujol (from  $+30$  to  $+100^\circ\text{C}$ ) as solvents. Solution spectra in  $\text{CS}_2$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_3$  of both compounds were obtained using 0.1 mm and 1 mm sealed cells.

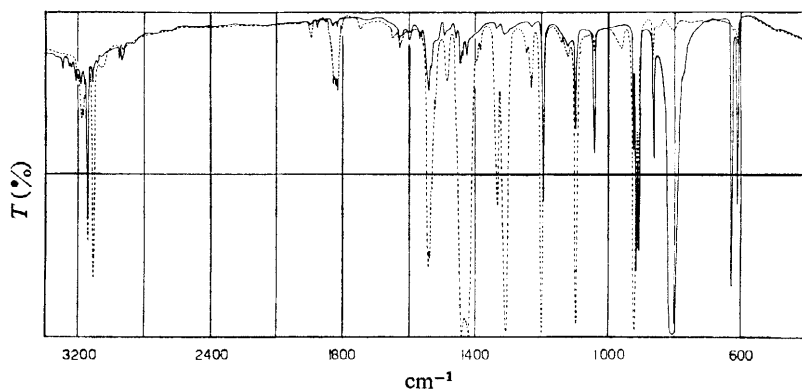


FIG. 2.—Infra-red spectrum in polarized light of 5,5'-bis-isoxazole- $\text{h}_4$ . Electric vector: — parallel to  $c$ ; - - - perpendicular to  $c$ .

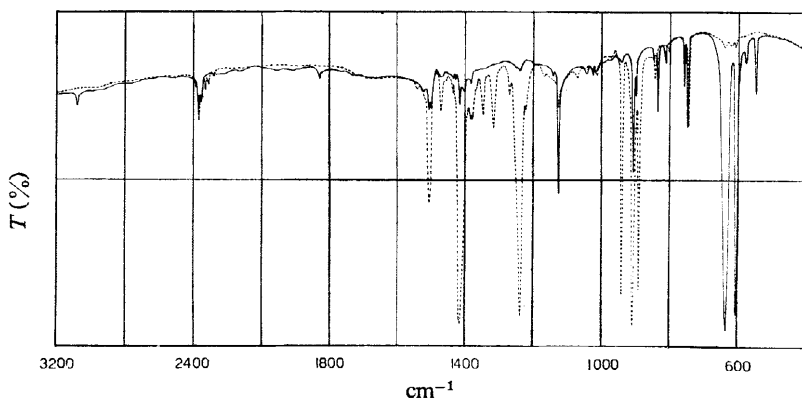


FIG. 3.—Infra-red spectrum in polarized light of 5,5'-bis-isoxazole- $\text{d}_4$ . Electric vector: — parallel to  $c$ ; - - - perpendicular to  $c$ .

Far infra-red spectra ( $200\text{--}70\text{ cm}^{-1}$ ) were measured with the aid of a Beckman IR-11 instrument in nujol mull and solution of benzene. Raman spectra of KBr pellets and powdered crystalline solid were obtained with a Cary-81 spectrometer using the method of

Ferraro and coworkers.<sup>13</sup> Raman spectra of solutions in  $\text{CHCl}_3$ ,  $\text{CS}_2$  and  $\text{CH}_3\text{CN}$  were also registered. Polarization data were measured using the conventional axial and cross polarizers. The spectra in polarized light of 5,5'-bis-isoxazole- $\text{h}_4$  and - $\text{d}_4$  are shown in fig. 2 and 3, respectively. The available spectroscopic data are summarized in tables 1 and 2.

The apparatus and techniques used for the determination of the dipole moment have been described elsewhere.<sup>14</sup> The measurements were made in benzene solution at 25°C.

TABLE 1.—VIBRATIONAL ASSIGNMENT OF 5,5'-BIS-ISOXAZOLE- $\text{h}_4$ 

| infra-red |    |          |          | Raman    |          | P  | assignment                                  |
|-----------|----|----------|----------|----------|----------|----|---|
| crystal   |    | liquid   | soln     | crystal  | soln     |    |   |
| [3 185 w  | ⊥  | 3 175 sh | —        | —        | —        | —  | 1 662 $A_g$ + 1 433 $B_u$ = 3 088 $B_u$     |
| [3 175 w  | ⊥  | —        | —        | 3 152 m  | 3 154 m  | p  | $A_g$ fundamental                           |
| 3 147 m   | np | 3 144 s  | 3 146 m  | —        | —        | —  | $B_u$ fundamental                           |
| 3 114 m   | ⊥  | 3 112 m  | 3 113 w  | —        | —        | —  | $B_u$ fundamental                           |
| —         | —  | —        | —        | 3 114 m  | 3 114 m  | p  | $A_g$ fundamental                           |
| 1 900 vw  | ⊥  | —        | —        | —        | —        | —  | 992 $A_g$ + 910 $B_u$ = 1 902 $B_u$         |
| 1 820 w   | ⊥  | —        | —        | —        | —        | —  | 1 433 $B_u$ + 387 $A_g$ = 1 820 $B_u$       |
| —         | —  | —        | —        | 1 676 vs | 1 671 vs | p  | [ $A_g$ fundamental in Fermi reson.         |
| —         | —  | —        | —        | 1 649 vs | 1 648 vs | p  | [with 1 277 $A_g$ + 387 $A_g$ = 1 664 $A_g$ |
| —         | —  | 1 562 w  | 1 567 w  | —        | 1 570 w  | —  | $A_g$ fundamental                           |
| [1 544 s  | ⊥  | 1 536 m  | 1 537 m  | —        | —        | —  | $B_u$ fundamental                           |
| [1 540 s  | ⊥  | —        | —        | 1 488 vs | 1 487 s  | p  | $A_g$ fundamental                           |
| 1 485 vw  | ⊥  | 1 477 vw | 1 475 vw | —        | —        | —  | 867 $A_u$ + 622 $B_g$ = 1 489 $B_u$         |
| [1 441 vs | ⊥  | 1 431 s  | 1 433 s  | —        | 1 427 w  | —  | [ $B_u$ fundamental in Fermi reson.         |
| [1 425 vs | ⊥  | 1 425 sh | 1 414 m  | —        | —        | —  | [with 818 $B_g$ + 612 $B_u$ = 1 430 $B_u$   |
| —         | —  | 1 349 m  | 1 350 w  | 1 355 m  | 1 357 m  | p  | $A_g$ fundamental                           |
| [1 334 m  | ⊥  | 1 336 w  | 1 336 w  | —        | 1 324 w  | —  | [ $B_u$ fundamental in Fermi reson.         |
| [1 309 s  | ⊥  | 1 308 m  | 1 309 m  | —        | —        | —  | [with 705 $B_u$ + 629 $A_u$ = 1 334 $B_u$   |
| —         | —  | —        | —        | 1 277 m  | 1 280 m  | dp | $A_g$ fundamental                           |
| —         | —  | 1 249 w  | 1 252 w  | —        | 1 257 w  | —  | $A_g$ fundamental                           |
| 1 246 vw  | ⊥  | —        | —        | —        | —        | —  | 629 $A_u$ + 622 $B_g$ = 1 251 $B_u$         |
| 1 232 w   | ⊥  | —        | —        | —        | —        | —  | 622 $B_g$ + 612 $A_u$ = 1 234 $B_u$         |
| [1 202 s  | ⊥  | —        | —        | —        | —        | —  |   |
| [1 196 m  |    | 1 192 s  | 1 192 s  | —        | —        | —  | $B_u$ fundamental                           |
| —         | —  | —        | —        | 1 198 m  | 1 197 m  | p  | $A_g$ fundamental                           |
| [1 101 w  |    | —        | —        | —        | —        | —  |   |
| [1 098 s  | ⊥  | 1 098 m  | 1 101 m  | —        | 1 099 w  | —  | $B_u$ fundamental                           |
| 1 043 m   |    | —        | —        | —        | —        | —  | $B_u$ fundamental                           |
| —         | —  | 1 028 m  | 1 025 m  | 1 038 m  | 1 031 m  | p  | $A_g$ fundamental                           |
| —         | —  | 990 m    | 990 vw   | 992 s    | 995 m    | p  | $A_g$ fundamental                           |
| 922 s     | ⊥  | 918 s    | 919 s    | —        | —        | —  | $B_u$ fundamental                           |
| 917 m     |    | 913 s    | 914 s    | —        | —        | —  | $A_u$ fundamental                           |
| —         | —  | —        | —        | 914 w    | —        | —  | $B_g$ fundamental                           |
| 910 s     | np | 910 sh   | 910 sh   | —        | —        | —  | $B_u$ fundamental                           |
| —         | —  | 885 w    | 892 m    | 890 s    | 894 m    | p  | $A_g$ fundamental                           |
| 867 m     |    | 862 w    | 863 m    | —        | —        | —  | $B_u$ fundamental                           |
| 810 vs    |    | 796 s    | 792 vs   | —        | —        | —  | $A_u$ fundamental                           |
| —         | —  | —        | —        | 818 w    | 813 w    | dp | $B_g$ fundamental                           |
| —         | —  | —        | —        | 705 w    | 712 w    | dp | $B_g$ fundamental                           |
| 629 s     |    | 631 w    | 631 w    | —        | —        | —  | $A_u$ fundamental                           |
| —         | —  | 622 w    | 623 vw   | —        | —        | —  | $B_g$ fundamental                           |
| 612 m     |    | 615 w    | 615 w    | —        | —        | —  | $A_u$ fundamental                           |
| —         | —  | —        | —        | 387 w    | —        | —  | $A_g$ fundamental                           |
| —         | —  | —        | —        | 331 w    | 325 w    | dp | $B_g$ fundamental                           |
| 156 m     | —  | —        | 140 m    | —        | —        | —  | $B_u$ fundamental                           |
| 104 m     | —  | —        | —        | —        | —        | —  | lattice mode                                |
| 82 w      | —  | —        | 82 w     | —        | —        | —  | $A_u$ fundamental                           |

w = weak, m = medium, s = strong, v = very, sh = shoulder, ⊥ = polarized perpendicularly to the  $c$  axis, || = polarized parallel to the  $c$  axis, np = non polarized, p = polarized, dp = depolarized.

## RESULTS AND DISCUSSION

### CRYSTAL SPECTRA

5,5'-bis-isoxazole crystallizes in the triclinic system,<sup>10</sup> space group  $P\bar{1}$  ( $C_i^1$ ) with two molecules in the unit cell, lying on  $C_i$  sites not related one to the other by factor group operations. Two sets of equivalent sites are therefore present and splitting

into two components of the infra-red and Raman bands is expected, because of the coupling between inequivalent molecules. The selection rules for the crystal (factor group  $C_i$ ) are shown in table 3.

TABLE 2.—VIBRATIONAL SPECTRUM OF 5,5'-BIS-ISOXAZOLE- $d_4$ 

| crystal  | infra-red   | soln      | soln Raman | P | assignment        |
|----------|-------------|-----------|------------|---|-------------------|
| —        | —           | —         | 2 362 w    | — | $A_g$ fundamental |
| 2 352 w  | $\perp$     | 2 348 (?) | —          | — | $B_u$ fundamental |
| —        | —           | —         | 2 343 w    | — | $A_g$ fundamental |
| 2 330 w  | np          | —         | —          | — | $B_u$ fundamental |
| —        | —           | —         | 1 649 s    | p | $A_g$ fundamental |
| —        | —           | —         | 1 621 w    | p | —                 |
| [1 508 m | $\perp$     | 1 494 m   | —          | — | $B_u$ fundamental |
| 1 500 w  | $\parallel$ | —         | —          | — | —                 |
| 1 474 w  | —           | —         | —          | — | —                 |
| —        | —           | 1 448 vw  | 1 457 m    | p | $A_g$ fundamental |
| 1 417 vs | $\perp$     | 1 410 vs  | —          | — | $B_u$ fundamental |
| 1 380 w  | $\perp$     | 1 390 sh  | —          | — | —                 |
| 1 348 w  | $\perp$     | —         | —          | — | —                 |
| —        | —           | 1 335 vw  | 1 344 vw   | p | $A_g$ fundamental |
| 1 318 w  | $\perp$     | —         | 1 312 w    | — | —                 |
| —        | —           | 1 301 vw  | —          | — | —                 |
| —        | —           | 1 285 vw  | —          | — | —                 |
| 1 272 vw | $\perp$     | —         | —          | — | —                 |
| 1 240 vs | $\perp$     | 1 243 m   | 1 242 vw   | — | $B_u$ fundamental |
| 1 225 sh | $\perp$     | 1 231 w   | —          | — | —                 |
| 1 128 m  | $\parallel$ | 1 127 m   | —          | — | $B_u$ fundamental |
| 941 s    | $\perp$     | 940 m     | —          | — | $B_u$ fundamental |
| 909 vs   | $\perp$     | 907 m     | —          | — | $B_u$ fundamental |
| 900 w    | np          | —         | —          | — | —                 |
| 891 s    | $\perp$     | 889 m     | —          | — | $B_u$ fundamental |
| [846 vw  | $\perp$     | 844 w     | —          | — | $B_u$ fundamental |
| 837 w    | $\parallel$ | —         | —          | — | —                 |
| 814 vw   | $\parallel$ | —         | —          | — | —                 |
| 806 vw   | $\perp$     | —         | —          | — | —                 |
| 760 w    | $\parallel$ | —         | —          | — | $A_u$ fundamental |
| [750 m   | $\parallel$ | —         | —          | — | $B_u$ fundamental |
| 746 m    | $\perp$     | —         | —          | — | —                 |
| 637 vs   | $\parallel$ | 631 m     | —          | — | $A_u$ fundamental |
| 607 vs   | $\parallel$ | 603 m     | —          | — | $A_u$ fundamental |
| 580 vw   | $\parallel$ | —         | —          | — | —                 |
| 552 w    | $\parallel$ | —         | —          | — | $A_u$ fundamental |
| 148 m    | —           | —         | —          | — | $B_u$ fundamental |
| 99 m     | —           | —         | —          | — | lattice mode      |
| 79 vw    | —           | —         | —          | — | $A_u$ fundamental |

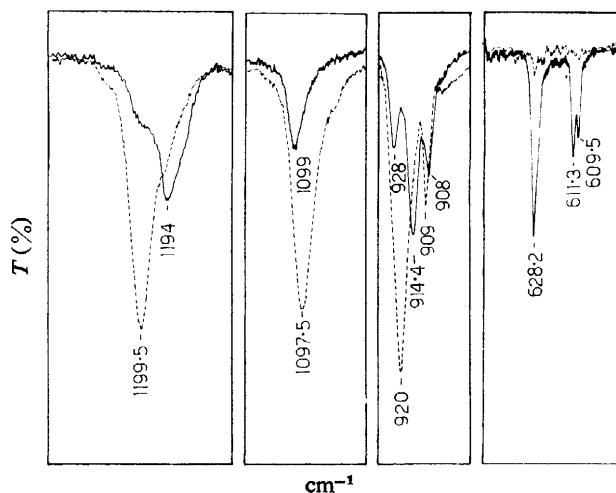
w=weak, m=medium, s=strong, v=very, sh=shoulder, polarized perpendicularly to  $c$  axis, polarized parallel to the  $c$  axis, np=non polarized, p=polarized

It follows that each molecular mode of the free molecule splits into two unit cell modes, both Raman active for  $A_g$  and  $B_g$ , both infra-red active for  $A_u$  and  $B_u$  fundamentals. The splitting due to the double multiplicity of the unit cell is experimentally verified for several bands which show two components in the spectra in polarized light at liquid nitrogen temperature (fig. 4).

TABLE 3.—CORRELATION DIAGRAM AND SELECTION RULES

| molecular group |     | site group |       | factor group |     |      |
|-----------------|-----|------------|-------|--------------|-----|------|
| act.            | nr. | $C_{2h}$   | $C_i$ | $C_i$        | nr. | act. |
| R               | 13  | $A_g$      | $A_g$ | $A_g$        | 36  | R    |
| R               | 5   | $B_g$      | $B_g$ | $B_g$        |     |      |
| IR              | 6   | $A_u$      | $A_u$ | $A_u$        | 36  | IR   |
| IR              | 12  | $B_u$      | $B_u$ | $B_u$        |     |      |

IR = infrared active, R = Raman active

FIG. 4.—Infra-red spectrum in polarized light of 5,5'-bis-isoxazole-h<sub>4</sub> at liquid nitrogen temperature. Electric vector: — parallel to *c*; - - - perpendicular to *c*.

## INFRA-RED SPECTRUM IN POLARIZED LIGHT

Trans planar 5,5'-bis-isoxazole belongs to the  $C_{2h}$  point group and accordingly its 36 normal modes classify as 13  $A_g$ , 5  $B_g$ , 12  $B_u$  and 6  $A_u$ . Since the centre of symmetry is preserved in the crystal, the mutual exclusion rule will still hold. We expect, therefore, only 18 fundamentals active in the infra-red spectrum and 18 active in the Raman spectrum. The interpretation of the i.-r. spectrum in polarized light is not straightforward. Two main difficulties are encountered, the first due to the triclinic symmetry and the second to the absence of precise informations about the orientation of the molecules in the sample.

In the triclinic crystal, the principal axis of the dielectric and polarizability tensors are not fixed by symmetry and can rotate with the wavelength. This effect can introduce strong variations in the polarization of bands of the same symmetry. For bis-isoxazole, however, it does not seem to play a significant role. All bands are strongly polarized in a consistent way and no detectable variation of the angle of maximum band polarization is observed over the whole frequency range. This is in agreement with the pseudo-orthorhombic structure found by the X-ray analysis and ensures a correct interpretation of the spectrum. As for the molecular orientation in the sample analyzed in polarized light, it is possible to prove that the *c* crystal axis lies in the film plane. 5,5'-bis-isoxazole crystallizes in needles elongated along the *c*

axis. We found that the direction of growth of the crystallites in the film plane coincides with the direction of maximum intensity of out-of plane modes. Since the molecules are packed in the crystal with the molecular plane almost perpendicular to  $c$ , this axis must lie in the plane. Spectra will be referred to as "parallel" (full line spectra) or "perpendicular" (dotted line spectra) according as they were registered with the electric vector parallel or perpendicular to  $c$ .

TABLE 4.—FUNDAMENTAL FREQUENCIES OF 5,5'-BIS-ISOXAZOLE- $\text{h}_4$  AND  $-\text{d}_4$ 

| species | no. | $\text{C}_6\text{H}_4\text{N}_2\text{O}_2$ | $\text{C}_6\text{D}_4\text{N}_2\text{O}_2$ | approximate description |
|---------|-----|--|--|-------------------------|
| $A_g$   | 1   | 3 152                                      | 2 362                                      | CH stretching           |
|         | 2   | 3 114                                      | 2 343                                      | CH stretching           |
|         | 3   | 1 662                                      | 1 649                                      | ring                    |
|         | 4   | 1 570                                      | —  | ring                    |
|         | 5   | 1 488                                      | 1 457                                      | ring                    |
|         | 6   | 1 355                                      | 1 344                                      | ring                    |
|         | 7   | 1 277                                      | —  | CH bending              |
|         | 8   | 1 257                                      | —  | CH bending              |
|         | 9   | 1 198                                      | —  | ring-ring stretching    |
|         | 10  | 1 038                                      | —  | ring                    |
|         | 11  | 992  | —  | ring                    |
|         | 12  | 890  | —  | ring                    |
|         | 13  | 387  | —  | ring-ring deform.       |
| $B_g$   | 14  | 914  | —  | CH bending              |
|         | 15  | 818  | —  | CH bending              |
|         | 16  | 705  | —  | ring                    |
|         | 17  | 622  | —  | ring                    |
|         | 18  | 331  | —  | ring-ring deform.       |
| $A_u$   | 19  | 917  | 760  | CH bending              |
|         | 20  | 810  | 637  | CH bending              |
|         | 21  | 629  | 607  | ring                    |
|         | 22  | 612  | 552  | ring                    |
|         | 23  | —  | —  | ring-ring deform.       |
|         | 24  | 82   | 79   | ring-ring torsion       |
| $B_u$   | 25  | 3 147                                      | 2 352                                      | CH stretching           |
|         | 26  | 3 114                                      | 2 330                                      | CH stretching           |
|         | 27  | 1 542                                      | 1 504                                      | ring                    |
|         | 28  | 1 433                                      | 1 417                                      | ring                    |
|         | 29  | 1 321                                      | 1 240                                      | ring                    |
|         | 30  | 1 199                                      | 941  | CH bending              |
|         | 31  | 1 099                                      | 891  | CH bending              |
|         | 32  | 1 043                                      | 1 128                                      | ring                    |
|         | 33  | 922  | 909  | ring                    |
|         | 34  | 910  | 748  | ring                    |
|         | 35  | 867  | 841  | ring                    |
|         | 36  | 156  | 148  | ring-ring deform.       |

Once the presence of the  $c$  axis on the film plane is established, we expect out-of-plane modes to be strong in the parallel and absent in the perpendicular spectrum. The behaviour of the in-plane modes depends on the second crystal axis present in the film plane. If the ( $ac$ ) plane is developed in our samples, in plane modes will behave as follows: (a) transition dipole parallel to the short molecular axis: strong on the perpendicular and absent in the parallel spectrum; (b) transition dipole parallel

to the long molecular axis: weak in the parallel and absent in the perpendicular spectrum, but strong in disordered sample spectra (KBr pellets); (c) orientation of the transition dipole intermediate between the two limiting cases above: polarization of the bands variable between the two limits. The above arguments should be reversed for the crystal (*bc*) plane and an intermediate situation should occur for crystal planes of the (*hkO*) type.

Inspection of the spectrum of fig. 2 shows that in-plane modes possess complete perpendicular polarization except for a few cases, viz., two bands with parallel polarization at 1043 and 867  $\text{cm}^{-1}$  and two non-polarized bands at 3147 and 910  $\text{cm}^{-1}$ . Their intensity increases strongly in the spectrum of a disordered sample (KBr pellets). The assignment of the infra-red modes becomes straightforward on the basis of the above discussion. All parallel bands, except the 1043 and 867  $\text{cm}^{-1}$  belong to the  $A_u$  species. All perpendicular bands as well as those at 3147, 1043, 910 and 867  $\text{cm}^{-1}$  belong to the  $B_u$  species. The spectrum of 5,5'-bis-isoxazole- $d_4$  closely resembles that of the light isotopic molecule. Again, only four in plane modes at 2352, 1128, 841 and 748  $\text{cm}^{-1}$  do not show complete perpendicular polarization and correlate with the corresponding four bands discussed above. All other bands have complete perpendicular polarization if belonging to in-plane or complete parallel polarization if originated by out-of-plane modes.

The vibrational assignment, together with an approximate description in terms of the usual group motions, is given in table 4. The band polarization is so characteristic that there is no need for discussion. Only for the low frequency region, where polarization measurements are not available, the assignment must be considered as tentative. We have chosen, by comparison with the assignment of biphenyl, the band at 154  $\text{cm}^{-1}$  as the in plane inter-rings scissoring mode and the band at 82  $\text{cm}^{-1}$  as the torsional vibration. In bis-isoxazole- $d_4$ , these bands are found at 148 and 79  $\text{cm}^{-1}$ . The corresponding torsional mode of biphenyl is infra-red inactive and its identification has required considerable effort. The localization of this vibration in bis-isoxazole is in contrast a simple matter.

Another band occurring at 104  $\text{cm}^{-1}$  in bis-isoxazole and at 99  $\text{cm}^{-1}$  in bis-isoxazole- $d_4$  was assigned to a lattice mode since this band disappears in the solution spectrum. The experimental isotopic rule for  $B_u$  species (3.83) compares well with the theoretical value (3.88).

#### RAMAN SPECTRUM

The Raman spectrum of crystalline bis-isoxazole- $h_4$  is reported in table 1. No coincidence with infra-red bands is observed, in agreement with the presence of a centre of symmetry. In order to assign the Raman bands to the proper symmetry species, we used essentially the correlation with the spectrum of the solution for which the depolarization factors were measured. This correlation implies either that no distortion occurs in solution or that the totally symmetric modes of the planar form correspond to totally symmetric modes of the distorted configuration eventually existing in solution. We prove later that in solution the molecular structure is actually distorted. However, the correlation among the modes in the crystal and in the solution is still significant since we expect, from the correlation diagram,  $A_g$  modes of the  $C_{2h}$  group to map into  $A$  modes of the  $C_2$  group. The latter is the group of symmetry to which any distorted configuration obtainable by a rotation around the C—C central bond, would belong.

Nine  $A_g$  modes are easily identified from their polarization. Another  $A_g$  fundamental is expected in the 400-300  $\text{cm}^{-1}$  range by comparison with biphenyl (360  $\text{cm}^{-1}$ ). We assigned this mode to the weak Raman band occurring in the crystal at 387  $\text{cm}^{-1}$ .



The remaining three  $A_g$  modes were tentatively assigned to the weak Raman bands at 1570, 1277 and 1257  $\text{cm}^{-1}$ .

Four of the five  $B_g$  modes are found in the Raman spectrum at 914, 818, 705 and 331  $\text{cm}^{-1}$ . The fifth mode of this species was not identified in the Raman spectrum. In the infra-red spectrum of the liquid, where  $g$  modes are expected to appear, a weak band is observed at 622  $\text{cm}^{-1}$  and could well fit the assignment for an out-of-plane mode.

The Raman spectrum of bis-isoxazole- $d_4$  was also measured. Owing to the small amount of compound available, only few of the most intense lines were detected. Their assignment is shown in table 2.

#### LIQUID PHASE SPECTRA AND DIPOLE MOMENT

The infra-red spectra of liquid 5,5'-bis-isoxazole (fig. 5) and of its solutions show a more complex pattern than that of the crystal. Several new bands, corresponding

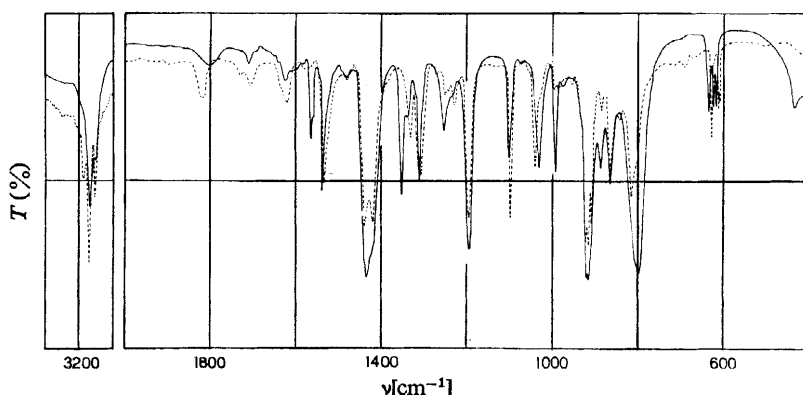


Fig. 5.—Spectrum of a liquid sample (—) of 5,5'-bis-isoxazole at 120°C and of the same sample after recrystallization (---).

to Raman active modes, appear, showing that the molecule has lost its centre of symmetry. The same effect is observed in the Raman spectrum where weak lines, corresponding to infra-red bands, can be detected. In order to ascertain whether one or more species were present in solution, we investigated the temperature dependence of the infra-red spectrum in the range +40 to +100°C. No variation in the relative

TABLE 5.—DIPOLE MOMENT EXPERIMENTAL AND EXTRAPOLATION DATA

| solvent : benzene | $\epsilon_1 = 2.271\ 89$ | $d_1 = 0.873\ 62$ | $n = 2.244\ 87$    |
|-------------------|--------------------------|-------------------|--------------------|
| $f_2$             | $\epsilon_{12}$          | $d_{12}$          | $\frac{n}{n_{12}}$ |
| 0.000 492 4       | 2.273 87                 | 0.873 81          | 2.244 59           |
| 0.001 016 1       | 2.277 53                 | 0.874 09          | 2.244 59           |
| 0.001 533 8       | 2.280 15                 | 0.874 37          | 2.244 59           |
| 0.001 776 2       | 2.278 32                 | 0.874 49          | 2.244 87           |
| 0.002 333 2       | 2.282 26                 | 0.874 81          | 2.245 16           |
| 0.002 792 3       | 2.283 93                 | 0.874 96          | 2.245 16           |
| 0.003 471 6       | 2.288 70                 | 0.875 35          | 2.245 44           |
| 0.004 145 8       | 2.291 99                 | 0.875 69          | 2.245 44           |

Extrapolation data:  $\epsilon'_1 = 2.271\ 6 \pm 0.000\ 7$ ;  $d'_1 = 0.873\ 57 \pm 0.000\ 01$ ;  $n_1'^2 = 2.244\ 42 \pm 0.000\ 06$ ;  $\alpha = 4.8 \pm 0.3$ ;  $\beta = 0.510 \pm 0.005$ ;  $\gamma = 0.27 \pm 0.02$ ;  ${}_\infty P_2 = 101 \pm 4$ ;  $MR_2 = P_E = 34.0 \pm 0.5$ ;  $\mu = 1.76 \pm 0.06$ .



intensity of the bands was observed. This proves the occurrence of only one molecular species in solution.

On the other hand, the frequencies and intensities of the infra-red and Raman bands in the liquid and solution spectra are close to those of the crystal. This implies the existence in the liquid phase of a distorted configuration nearer to the trans than to the cis form. The lack of the centre of symmetry is also confirmed by our measurement, in solution of benzene at 25°C, of the dipole moment of 5,5'-bis-isoxazole, for which we found a value of 1.76 D (see table 5). Once the presence of only one conformation in solution is established, from this value of  $\mu$  an angle between the ring planes of 44° can be calculated, assuming 2.81 D<sup>14</sup> for the isoxazole moment and full vectorial additivity of the ring moments. This is only a rough indication of the situation in solution, but it is sufficient to indicate the occurrence of a noticeable distortion from planarity. Similar values of the inter-planar angles have also been found for biphenyl and bipyridyl by electron diffraction studies.<sup>4</sup> Moreover, preliminary results obtained by n.m.r. spectra of 5,5'-bis-isoxazole in the nematic phase seem to agree with the above interpretation.<sup>15</sup>

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