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Polarized Infrared Spectra of Tolane Single Crystal*

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Polarized infrared spectra of an oriented and very thin tolane crystal have been measured in the 3500—50 cm^{-1} region. The symmetry of the infra red active internal vibrations is proposed on the basis of the oriented gas model. The application of the vibrational spectroscopy in studying the conformation of the free tolane molecule is discussed.

INTRODUCTION

The conformation of non-rigid molecules containing phenyl rings has attracted the attention of spectroscopists in recent years. The problem of the conformation of the tolane molecule has been raised from the first crystal structure analysis performed by Robertson and Woodward¹. Later structural investigations^{2,3} have shown that the unit cell consists of two crystallographically non-equivalent sets of molecules with similar bond distances and angles, but differing in orientation. The origin of such a relationship in the tolane crystal is still unclear.

While the molecules in the crystal are plane within experimental errors, the conformation of the free molecule has not been established yet. In order to investigate this problem, quantum-mechanical calculations were carried out⁴, and the energy barrier thus obtained (2.7 kJ/mol) corresponds to a quasi free rotation of the phenyl rings around the C—C single bonds. Our aim is to study this conformational problem by vibrational spectroscopy techniques and using normal coordinate analysis. The large number of vibrational frequencies of this molecule requires an approach by different methods. Above all it is advisable to proceed very gradually.

In the present paper we report results of the vibrational analysis performed on the tolane single crystal, which enabled us to determine the symmetry of the internal vibrational modes.

Molecular and Crystal Structure

Tolane crystallizes in a monoclinic system, space group $P2_1/a$ with $Z = 4$ molecules in the unit cell³. The molecules belonging to each set are packed

* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

in layer along the crystallographic c-axis (Figure 1). The site symmetry of both non-equivalent toluene molecules is C_i . Their structures are the same with approximate D_{2h} symmetry.

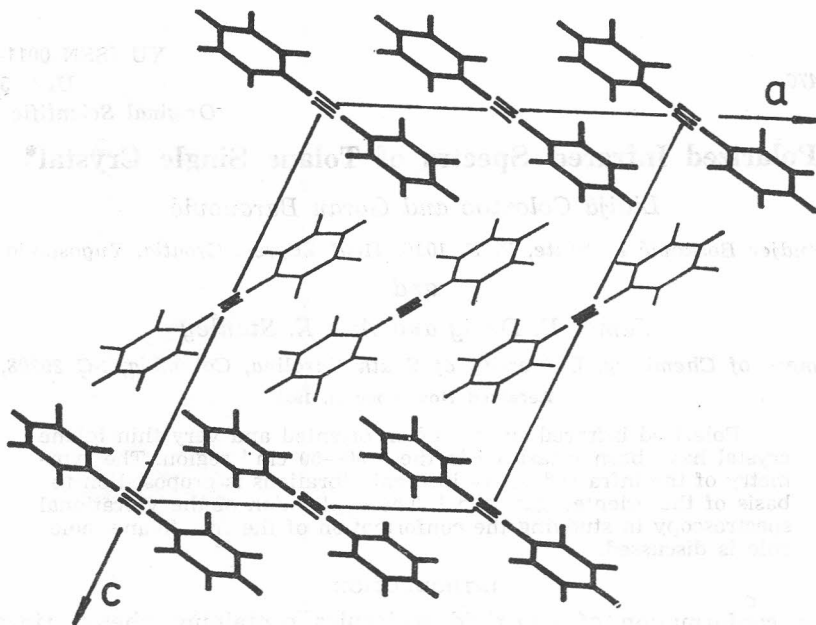


Figure 1. Crystal structure of toluene

The correlation between the molecular groups, site groups and factor groups (Table I) indicates that the total number of internal vibrations in the

TABLE I

Selection Rules and Symmetry of Molecular and Crystal Vibrations

Molecular group	Site group	Factor group
	D_{2h}	C_{2h}
$12\nu^a$	a_g	A_g $2 \times 33\nu, 6 R_i$
$3\nu, R_L$	b_{1g}	$33\nu, R_i$ A_g
$7\nu, R_M$	b_{2g}	
$11\nu, R_N$	b_{3g}	
4ν	a_u	A_u $2 \times 33\nu, 5 T_i$
$11\nu, T_L$	b_{1u}	$33\nu, T_i$ A_u
$11\nu, T_M$	b_{2u}	
$7\nu, T_N$	b_{3u}	

^a ν stands for the vibrational frequencies

crystal unit cell is 264. In fact, each internal vibration should in principle be doubled in each factor group on account of the two sets of molecules. At room temperature this doubling is not observed. Thus the total number of observed bands is practically reduced by half. One of the possible explanations for this feature will be offered later on in this paper. With regard to the lattice vibrations, we obviously have to consider all four molecules and consequently there are 21 lattice vibrations.

EXPERIMENTAL

Single crystals of tolane were grown from melt by slow cooling. Large and clear single crystals were optically oriented by observing interference patterns in a polarizing microscope. Observation of X-ray diffraction in an oriented sample established that the axis of the lowest refractivity is parallel to the crystal binary axis *b*.

The sample for IR absorption measurements must be oriented against the refractivity axes in order to conserve the linear polarization of the incident beam inside the crystal. The preparation of oriented and enough thin samples is the most difficult part of this type of experiments. The necessary thinness of the sample can be obtained only if the single crystal is attached to the support - window. Any kind of glue would give its own spectrum and therefore it is better not to use it. We have solved this problem by attaching the crystal sample to the support by melting a very thin layer of the crystal in front of the window. If the layer of the melt is very thin in comparison to the thickness of the whole crystal, and if the cooling of the support and the crystal is performed slowly, the molten part of the crystal will recrystallize in a perfect single crystal. This can be verified by observing the extinction of polarized light. If the thinning is performed by rubbing the crystal on a wet silk, the deposition of the material around the sample will fasten the crystal more securely to the support. This feature makes it possible to prepare very thin single crystals. The same procedure can be used even for FIR measurements. The only limit is set by the melting-point of the polyethylene windows.

The spectra measured in the middle infra red region have been recorded with a Perkin Elmer 650 spectrometer (Figure 2.), while the FIR spectra were recorded with a Digilab FTS-15B Fourier transform interferometer. The polarization of the incident beam in the middle infra red region was ensured by a polarizing filter, while the polarization in FIR interferometer was obtained on the Mylar beamsplitter only.⁵

INTERPRETATION OF THE OBSERVED SPECTRA

The notion of characteristic frequencies of functional groups like phenyl rings is particularly helpful in the assignment of the vibrational spectra. The correlation between the point group D_{6h} of benzene and the group C_{2v} , which is the point group for one half of the tolane molecule, enables us to derive the symmetry of the ring vibrations in tolane. However, the number of frequencies observed in the Raman as well as in the IR spectrum is still very large, and furthermore, these frequencies can be very close. Polarization analysis of scattered light (Raman) or of absorbed light (IR) offers a further experimental possibility of separating transition moments of different symmetry, even in the case of very close frequencies.

The number of vibrations and the symmetry species in the crystal spectrum can be derived from the correlation between the molecular group, site group and factor group given in Table I. From this correlation it follows that all molecular vibrations of the «u» species will be active in both the A_u and B_u spectrum of the crystal. The molecular modes of the b_{1u} and b_{2u} species describe in-plane vibrations with the transition moment oriented along the longest (L) and middle (M) molecular axes respectively. The transition moment

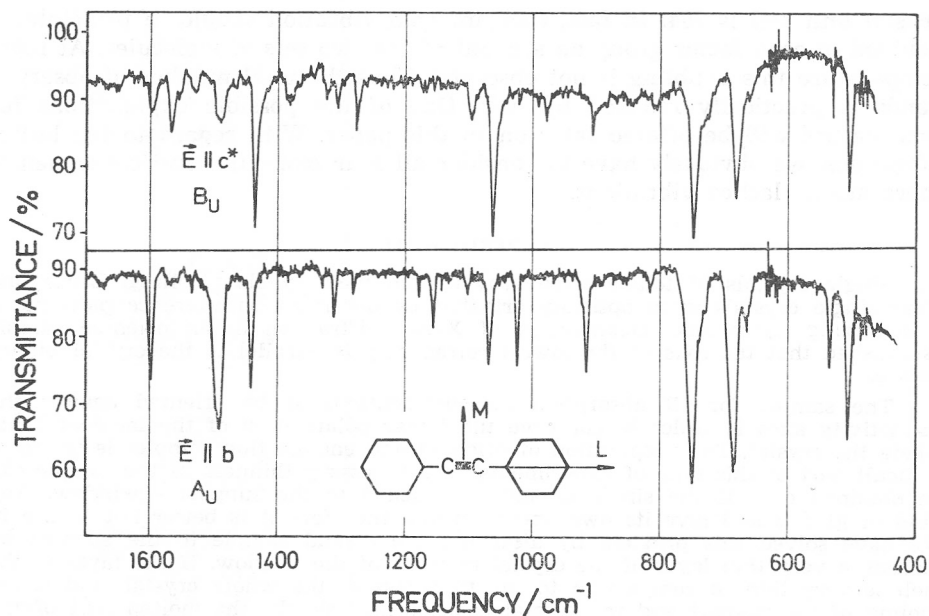


Figure 2. Polarized IR spectra of a thin tolane single crystal and the definition of the molecular axes. The polarizations used: $\vec{E} \parallel b$ (A_u), $\vec{E} \parallel c^*$ (B_u).

of the vibrations of the species b_{3u} is normal (N) to the molecular plane. The definition of the molecular axes is given in Figure 1. The vibrations of the species a_u , which are forbidden in the molecular group D_{2h} , become active in the crystal spectrum. The corresponding bands can be detected by comparison of the spectrum of the crystal to the spectrum of solution or vapor, where these bands must be absent if the free molecular group is D_{2h} .

Oriented gas approximation has been often applied in the determination of the symmetry species of the IR active vibrations in the crystal.⁶ In this approximation the interaction between the molecules in the lattice is neglected and the intensity of the absorbed band is proportional to the square of the direction cosine between transition moment and the principal axes of the optical indicatrix (a^* , b , c^*). The angles of the molecular axes in the frame of the crystallographic axes are given by X-ray analysis. In the case of monoclinic crystals, the angles between the crystallographic and the principal axes of the optical indicatrix can be measured on an oriented sample with a polarizing microscope by observing along the binary axis and by measuring the angle between the layers of the cleavage planes and the direction of optical extinction. With respect to the crystal axes as defined in Ref. 3, a^* and c^* lie in the ac plane with a^* 5° from a and c^* 18° from c ; a^* , b and c^* are mutually orthogonal.

Since the measurement is performed on the crystal sample, the vector of the incident radiation will be interacting with the total dipole moment of the crystal which in the present model corresponds to the sum of dipoles of all molecules in the crystal. Consequently, if we apply the oriented gas approximat-

ion to tolane, we have to take into account that there are two sets of molecules. From the positions of the two non-equivalent molecules in the frame of the principal axes of the optical indicatrix (see Tables IIa and IIb) we calculated the intensity matrices for the internal modes.

TABLE II

The Matrices Φ_1 and Φ_2 of the Direction Cosines of the Two Non-equivalent Tolane Molecules^a

a)	Φ_1	L	M	N
	a^*	0.845	-0.417	-0.318
	b	0.269	0.852	-0.462
	c^*	0.462	0.315	0.827
b)	Φ_2	L	M	N
	a^*	0.783	0.338	0.499
	b	-0.101	0.892	-0.446
	c^*	-0.614	0.299	0.743

^a L, M, N are the molecular axes. a^* , b, c^* are the principal axes of the optical indicatrix.

As it was already emphasized (see correlation Table I), a doublet of bands corresponds to each internal mode for a given crystal symmetry class. Since both sets of molecules have a common binary axis b, the calculation performed showed, that if the intensity of one component of that doublet is proportional to the square of the sum of the direction cosines:

$$I_1 \sim |\Phi_{1,ij} + e^{i\varphi} \Phi_{2,ij}|^2 \quad \begin{array}{l} i = a^*, b, c^* \\ j = L, M, N \text{ or } b_{1u}, b_{2u}, b_{3u} \end{array}$$

then the intensity of one other is proportional to the square of the difference of the same cosines:

$$I_2 \sim |\Phi_{1,ij} - e^{i\varphi} \Phi_{2,ij}|^2,$$

where $e^{i\varphi}$ is the phase difference of the two nonequivalent molecules which is a priori unknown. To avoid this complication we suppose (which is consistent with the general pattern of the spectra) that the frequency difference between the two components is small so that we actually see the superposition is small so that we actually see the superposition of the bands (or their intensities). The dichroic ratio (the relative intensity of the A_u to the B_u component), $\rho(j)$, is then simply:

$$\rho(j) = \frac{|\Phi_{1,2j} + e^{i\varphi} \Phi_{2,2j}|^2 + |\Phi_{1,2j} - e^{i\varphi} \Phi_{2,2j}|^2}{|\Phi_{1,3j} + e^{i\varphi} \Phi_{2,3j}|^2 + |\Phi_{1,3j} - e^{i\varphi} \Phi_{2,3j}|^2} = \frac{\Phi_{1,2j}^2 + \Phi_{2,2j}^2}{\Phi_{1,3j}^2 + \Phi_{2,3j}^2}$$

$$j = b_{1u}, b_{2u}, b_{3u}.$$

This gives $\rho(b_{1u}) = 0.14$, $\rho(b_{2u}) = 8.14$ and $\rho(b_{3u}) = 0.34$, and means, for example, that intensities of the b_{1u} bands should rise remarkably on changing the polarization of the spectrum from A_u to B_u . How these predictions are fulfilled can be seen from the Table III. The assignment of internal vibrations given the-

TABLE III

The Observed and Calculated Dichroic Ratios for Some Vibrational Modes of the Toluene Molecule

point group symmetry	Wilson notation	Obs. frequencies in cm^{-1}		dichroic ratio	
		(A_u)	(B_u)	obs.	calc.
b_{1u}	8a	1599	1594	0.71	
	19a	1490 doublet	1491 doublet	0.71	
	9a	1172	1173	0.67	0.14
	18a	1020	1021	0.30	
	12	992	994	5.01	
b_{2u}	8b	1568 doublet	1568	3.33	
	19b	1438	1439	1.00	8.14
	9b	1154	1150	0.11	
	18b	1064 doublet	1067	1.12	

rein was previously established by investigation of the Raman and infrared spectra of solutions. Obviously, the agreement is only qualitative for the majority of vibrational modes. For the oriented gas model with its well known deficiencies one could hardly expect more. Applying the same considerations to all observed bands we could determine the symmetry of each molecular vibrational mode active in the IR spectrum as given in Table IV. One of the deficiencies of the oriented gas approximation is that there exists no rule for the determination of the intensity distribution for the a_u internal modes, but it can be compensated by other types of measurements.

In Table IV we listed the frequencies of bands observed in the IR spectra of two polarizations for the single crystal samples of different thickness in order to demonstrate the dependence of the relative intensities on the thinness of the sample. Only the spectral region corresponding to the characteristic frequencies of the organic compounds is considered. We also give the spectrum of solution, which can be useful in further determination of the symmetry of some particular modes.

CONCLUSION

By determination of the symmetry species of each IR active vibrational mode, one of the necessary conditions is created for performing the normal coordinate calculations for large molecules like toluene. Other procedures such as comparison to similar molecules (phenylacetylene, biphenyl) or isotopic substitution can be used to improve the preliminary assignment of the observed spectrum and consequently to obtain the most reliable force field for the molecule of toluene. Only then will it be possible to attempt, a solution to the problem of the conformation of these molecules in solution. We are aware of the fact that the present results, although undoubtedly useful, are not

TABLE IV

Oriented Gas Approximation Applied to the Tolane Spectrum

Solution (cm ⁻¹)	C R Y S T A L (cm ⁻¹)				Symmetry
	<i>E</i> <i>b</i> (A _u)		<i>E</i> <i>c</i> * (B _u)		
	Thick	Thin	Thick	Thin	
3090S ^a		3085vS			b _{2u}
3070S		3068S		3068vS	b _{1u}
3042mS		3048m			b _{2u}
3030w		3030w		3036S	b _{1u}
		3032S		3023w	b _{2u}
1608vS	1599S	1599mb	1594vS	1601S	b _{1u}
1572m	1567vS	1569mS	1568m	1570w	b _{2u}
	1530m	1530wb	1529w	1535w	combination
1500vS	1495	1495sh	1495sh	1498S	b _{1u}
1492sh	1488 vS	1490m	1492vS	1492vS	b _{1u}
1446vS	1438vSb	1439vS	1439vSf	1443mf	b _{2u}
1435sh	1420sh	1425sh			b _{2u}
1382m	1382mSb	1384m	1382w		b _{2u}
1328w	1326Sf	1325m	1327mS	1330w	b _{2u}
1310S	1305Sf	1306w	1308vSf	1312m	b _{1u}
1280m	1276vS	1278mS	1275mS	1280w	b _{2u}
solvent			1328w		b _{1u}
solvent	1220w		1222sh		?
1179w	1172mS	1170vw	1175S	1179w	b _{1u}
1160w	1153w		1150vS	1158Sm	b _{3u}
1100m	1098m	1095m	1098m	1102w	b _{2u}
1070vS	1068sh		1067vS	1070S	b _{3u}
	1064vS	1065vS		1063sh	b _{2u}
1028S	1020m	1020vw	1021vS	1027S	b _{1u}
solvent	992m	992vw	992vw		b _{2u}
	980S	980m	980m		absent in solution, a _u ?
916S			912vS	918vS	b _{3u}
?	905S	908m			b _{2u}
	898w		890mw		absent in solution, a _u ?
878w	868m		868w		combination, b _{2u}
848m	845m	845w	850mS	850vw	combination, b _{1u}
solvent			815m	815m	b _{3u}
760vS	750vSb	750S	752vvS	752vS	b _{1u}
		735sh	745vS	740sh	combination, b _{1u}
		725sh	740sh	730sh	combination, ?
699sh			689vS	680vS	b _{3u}
690vS	682vS	682vS	685vS		b _{2u}
670m	660mw	660m	665S	665mw	b _{1u}
630w			620w		combination, ?
539S	534mw	530m	530vS	535S	b _{3u}
512S	505vS	505S	502vS	505vS	b _{3u}
	463vS	463S	462m	462w	absent in solution, a _u ?
400vS ^b		405m ^b		405m ^b	?
284sh ^b		288m ^b		288S ^b	b _{3u}
255m ^b		253w ^b		258m ^b	b _{3u}

^a S, m, w, v, b, f, sh denote strong, medium, weak, very, broad, sharp, shoulder respectively. ^b FIR measurements.

sufficient in themselves for a appropriate solution in vibrational spectroscopic studies on molecular conformations.

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SAŽETAK

Spektri tolana

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Polarizirani infracrveni spektri orijentiranog i vrlo tankog kristala tolana mjereni su u području od 3500 do 50 cm^{-1} . Infracrveno-aktivne interne vibracije razvrstane su po simetrijskim klasama na temelju modela orijentiranog plina. Rasprostrana je primjena vibracijske spektroskopije pri proučavanju konformacije slobodne molekule tolana.