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Assignment of the Lowest Singlet and Triplet States of the Monoaldehyde of Durene

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Abstract—The monoaldehyde of durene has been synthesized. It has been shown to be the impurity frequently encountered in spectral studies involving durene crystals. Both the polarized absorption and emission spectra of the protonated and deuterated aldehyde in crystals of durene$_{h-14}$ and durene$_{d-14}$ have been obtained. Although the lowest excited singlet and triplet states, separated by 2200 cm^{-1}, are shown to be $n\pi^*$ a number of features in the phosphorescence spectrum are more characteristic of a $^3\pi\pi^*$ state. The polarization of the absorption spectrum, in particular the 0–0 band and bands involving the excitation of totally symmetric vibrations, is inconsistent with the $n\pi^*$ nature of the transition. A number of explanations is proposed.

1. Introduction

The characterization and identification of the lowest, spectroscopically accessible singlet and triplet states of aromatic carbonyl compounds have evoked considerable current interest. Detailed investigations have been carried out on the ordering of the $n\pi^*$ and $\pi\pi^*$ states within the singlet and triplet manifolds and on the spin-orbit coupling mechanisms responsible for the radiative and radiationless spin-forbidden transitions.[1–10]

General interpretations of the accumulated results indicate that the experimentally measured transition polarizations, the vibrational envelopes and the magnitudes of the zero-field splittings, in the case of triplet states, are important criteria in ascertaining the natures of electronically excited states. It is in this context that the present study was undertaken.

The existence of an impurity emission in durene, which has not

been satisfactorily purified, has been recognized for some time.[11,12] On the basis of the emission spectrum, it has been assigned to an aldehyde oxidation product of durene. Recently Sharnoff[13] has determined the zero-field splitting parameters of the triplet state and has obtained confirmation that the species responsible for the emission is a monoaldehyde of durene and that the character of the emitting state is $^3n\pi^*$.

Yet the evidence supporting the $^3n\pi^*$ assignment is inconclusive insofar as the shape of the vibrational envelope is concerned. The vibrational fine structure is far more characteristic of the $^3\pi\pi^*$ phosphorescence of both 1- and 2-naphthaldehyde[2,8] than of the $^3n\pi^*$ emission of benzaldehyde.[2]

These observations have made it imperative to establish the exact identity of the emitting species with a view to pursuing a study of the optical absorption and emission spectra, in particular the transition polarizations and the dominant vibrational modes. It should also be pointed out that the majority of studies on transition polarizations of aromatic carbonyl compounds have been carried out in rigid glasses and on pure crystals and that the present mixed crystal study provides an addition to these.

The site symmetry of durene is C_i. Durene is a monoclinic crystal $P2_1/a$ with two molecules per unit cell.[14] The squared projections of the molecular axes on to the crystal axes are given in Table 6a. Since adjacent methyls in durene are not related by a centre of inversion, the spectra of the two possible aldehydes, obtained by replacement of the methyl by aldehyde, will display a site splitting. This may be manifested, as in the case of phenanthrene in biphenyl,[15] as a doubling of all bands with different transition polarizations for the two members of the doublet. No observations of this splitting have been reported by Sharnoff,[13] but for a similar mixed crystal, quinoline in durene,[16] a splitting has been observed in the ESR.

2. Experimental

The monoaldehyde of durene, 2,4,5-trimethylbenzaldehyde, was prepared by the controlled oxidation of durene with ceric salt in acid solution.[17] A solution of durene (1 m M) in acetic acid (50%) was

added dropwise, over a period of 4 hours, to a solution of ceric ammonium nitrate (2 mM) in acetic acid (50%) at 50 °C. The resulting aldehyde was purified by bisulphite extraction and vacuum sublimation. A melting point of 40 °C was obtained. Both NMR and mass spectrometry indicated a monoaldehyde of durene and indicated the absence of any bialdehyde. The 2,4,5-trimethylbenzaldehyde$_{d-12}$ was obtained by the same procedure from durene$_{d-14}$ and fully deuterated acetic acid. Under more extreme conditions of temperature and ceric concentration more than one methyl group may be oxidized.

After vacuum sublimation and zone refining, the durene$_{h-14}$ (Fluka Purum) and durene$_{d-14}$ (Isomet) gave no spectroscopic evidence of impurities. Crystal specimens with the *ab* face developed were obtained from cleavage sections and the *a* and *b* axes clearly identified conoscopically. Crystals with the *bc'* face developed were cut from *ab* cleavage specimens.

The spectra, of the melt-grown crystals (0.05 to 1 mole %) immersed in liquid helium, were recorded in the 1st order of a 1180 line/mm grating blazed at 5000 Å of a 3.4m Jarrell-Ash spectrograph. Calibration was with a hollow iron cathode and wavelengths could be measured to within 0.1 Å. Microdensitometer tracings were recorded with a Joyce-Loebl. The relative intensities were determined from the band heights and are estimated to be accurate to only within 20%. In ascertaining the relative intensities, no account was taken of the associated phonon structure. This is of little consequence in the phosphorescence spectra since the contribution of the accompanying phonons to the emission intensity is almost negligible. For the absorption spectra the intensity of absorption by phonons generally appeared proportional to the intensity of the respective vibronic band and thus could be ignored.

The axis designation is shown in Fig. 1 and follows the convention for C_{2v} molecules. Since trimethylbenzaldehyde does not belong to the C_{2v} symmetry group designation, a C_2 axis is not defined. However, descriptions in which (i) a C_2 axis is taken along the ring-*CO* axis reflecting the dominant perturbation of the aldehyde group on the ring, and (ii) a C_2 axis along the carbonyl bond reflecting the, perhaps, localized nature of $\pi^* \leftarrow n$ carbonyl transitions, have some merit in discussing the in-plane polarizations. The direction of the

normal is independent of the choice of C_2 axis and is strictly defined for a planar molecule. This is relevant to the 0–0 band and totally symmetric vibrations in the absorption spectrum.

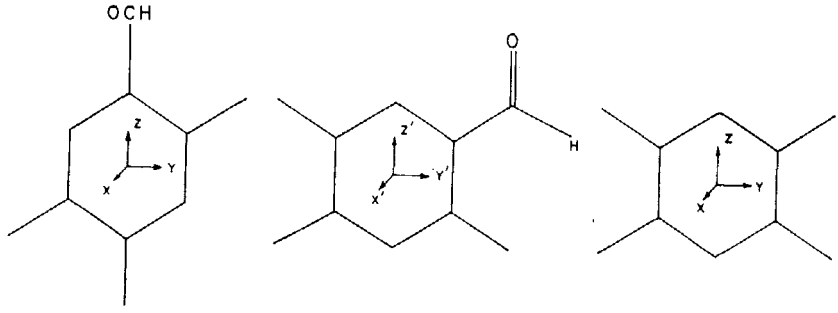

Figure 1. Axis designation. The x (x') axis is perpendicular to the molecular plane. For the xyz system of axes, two inequivalent crystal structures exist corresponding to the CHO group being in either of two adjacent positions, see Table 6a.

3. Crystal Spectra

I. Absorption

The polarized absorption spectrum at 3800 Å of trimethylbenzaldehyde in durene appears mainly as a short progression in the carbonyl stretching mode (h-12 1313, d-12 1296 cm^{-1}) based on the origin and polarized parallel to the crystal a axis. The absorption spectra of the aldehyde in its fully protonated and deuterated forms in crystals of durene$_{h-14}$ and durene$_{d-14}$, were recorded at 4 °K. Typical spectra, with incident light normal to the ab and bc' crystal planes, are shown in Figs. 2 and 3. More than half of the intensity is associated with the allowed electronic transition. A number of bands appear in the spectrum with different polarization behavior to the uniquely a-polarized origin band. Most prominent among these is a low frequency vibration of 235 cm^{-1} (d-12 204 cm^{-1}), assigned, by comparison with the benzaldehyde vapour spectrum,[18] to a vibration in which the —CHO group moves out of plane as a whole. Another vibrational mode also believed to be active in Herzberg-Teller coupling has a frequency of 693 cm^{-1} (for d-12 702

cm^{-1}). A vibration of 732 cm^{-1} (d-6 726 cm^{-1}) observed for benzaldehyde had been tentatively assigned to a ring vibration, correlating with a mode which has b_1 symmetry in C_{2v} monosubstituted benzenes. This would explain the different polarizations of the 693 and the 235 cm^{-1} modes both of which are a'' under C_s symmetry but correlate with b_1 and a_2 modes and induce intensity stealing from B_2 and A_1 states respectively in C_{2v} symmetry.

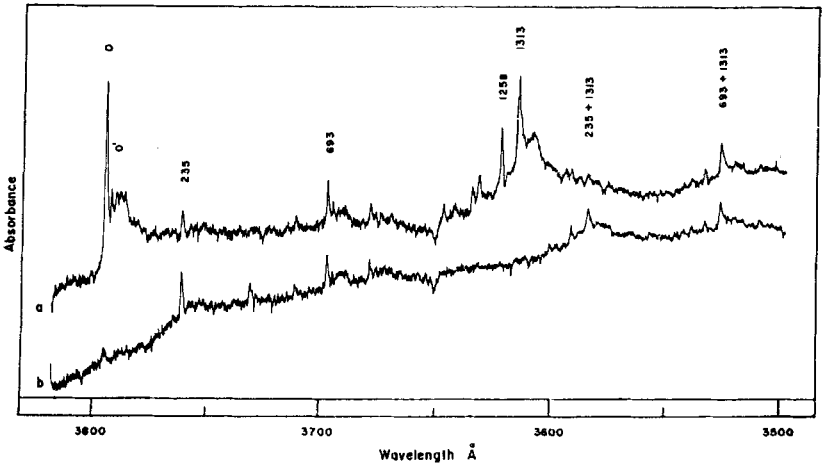

Figure 2. The absorption spectrum of 2,4,5-trimethylbenzaldehyde$_{h-12}$ in durene$_{h-14}$ parallel to the a and b axes at 4 °K.

Most bands in the spectrum appear as doublets with separations of 17 cm^{-1} (d-12 20 cm^{-1}). The high frequency member of the doublet is generally of reduced intensity and of different polarization. Thus for the 0–0 band the a/c' polarization ratios for the low and high frequency members of the doublet are 10 and 1.6 respectively. A list of the frequencies of the observed bands, their probable assignments and relative intensities are presented in Tables 1 and 2. Complete deuteration of the aldehyde shifts the origin by 62 cm^{-1} to the blue. No shift is observed upon deuteration of the durene host. For the intense bands in the spectrum a number of associated lattice modes are identified. Individual peaks at approximately 31, 44, 58 and 116 (2×58?) cm^{-1} are resolved for the h-12 aldehyde in the durene$_{h-14}$ host, and 27, 56, and 105 for the h-12 aldehyde in the durene$_{d-14}$ host.

The spectrum is typical of an $\pi^* \leftarrow n$ transition of an aromatic

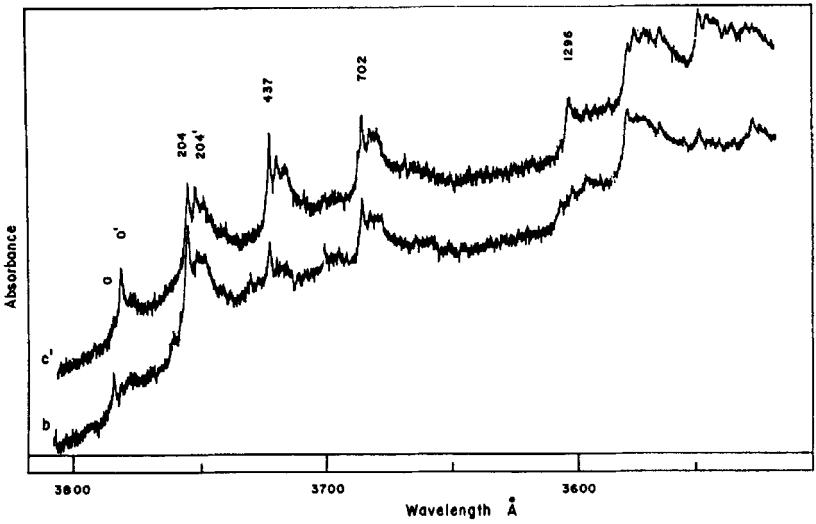

Figure 3. The absorption spectrum of 2,4,5-trimethylbenzaldehyde$_{d-12}$ in durene$_{h-14}$ parallel to the b and c' axes at 4 °K.

carbonyl. In durene host crystal the next highest singlet lies more than 5000 cm^{-1} to higher energies. For comparison the frequencies, extinction coefficients of the band maxima and oscillator strengths in n-hexane at 20 °C are recorded in Table 3.

II. Phosphorescence

The emission is designated phosphorescence on the basis of its lifetime, its polarization and its energy separation from the 0–0 band in absorption. These properties are later discussed in detail. The emission spectrum is identical with that previously reported[11,12] and is of the same lifetime.[13]

The most intense bands in the spectrum are the 0–0 band and a band assigned to the excitation of the aldehyde C—H out-of-plane wagging mode in the ground state. This mode has a frequency of 988 cm^{-1} for the h-12 aldehyde and 853 cm^{-1} for the d-12. Similar vibration frequencies are obtained for 2-naphthaldehyde[8] (980 ± 50 and 780 ± 50 cm^{-1}) and for planar aliphatic aldehydes such as propynal[19] (981 and 841 cm^{-1}) and propenal[20] (980 and 846 cm^{-1}). The carbonyl stretching mode (1684 h-12, 1670 d-12) is again active in the spectrum, but only one quantum is readily identified. Typical

TABLE 1 Vibrational Analysis and Relative Intensities Parallel to a, b and c' axes for 2,4,5-trimethylbenzaldehyde$_{h-12}$ in durene$_{h-14}$, in absorption

Frequency (cm^{-1})	Rel. Int. a	b	c'	Assignment	Frequency (cm^{-1})	Rel. Int. a	b	c'	Assignment†
26350	8.2	0.3	0.8	0	27898	0.6	0.8	0.8	$1313+235$ a''
26367	2.5	0	1.5	0^1	27921	0	0	0.9	$1313+235^1$ a''
26585	1.4	2.1	1.3	235 a''	28054	0	0	0	$1258+448$
26608	0.6	0.5	1.1	235^1 a''	28113	0	0	0	$1313+448$
26798	0.5	0.7	0	448	28178	0	0	0.8	$1313+517$
26816	0.4	0.3	0	448^1	28202	0	0	0	$1258+596$
26867	0	0	1.1	517	28256	0.5	0	0	$1313+596$
26885	0	0	0.5	517^1	28301	0.6	0.3	0.6	$1258+693$ a''
26939	0.7	0.5	0	589	28357	1.1	0.9	0.6	$1313+693$ a''
26956	0.1	0.1	0	589^1					
27043	1.7	1.2	1.1	693 a''	28441	0	0	0	$1258+830$
27060	0.8	0.4	1.0	693^1 a''	28497	0	0	0	$1313+830$
27180	1.2	0.9	0.6	830	28678	0	0	0	$1258+1067$
27196	0.5	0.3	0.4	830^1	28734	0.5	0	0	$1313+1067$
27417	1.2	0	0	1067	28770	0.6	0	0	$1258+1162$
27452	1.1	0	0	1102	28794	0.5	0	0	$1258+1186$
27512	1.1	0	0	1162	28826	0.5	0	0	$1313+1162$
27536	1.0	0	0	1186	28852	0.7	0	0	$1313+1186$
27608	2.9	0	0.5	1258 a'	28866	0.7	0	0	2×1258 a'
27625	0.9	0	0.6	1258^1 a'	28919	1.2	0	0	$1313+1258$ a'
27663	3.3	0	0.5	1313 a'	28972	1.0	0	0	2×1313 a'
27680	0.6	0	0.6	1313^1 a'	29210	0.8	0	0	$2\times1313+235$ a''
27840	0.5	0.8	0.6	$1258+235$ a''	29609	0.6	0.3	0	$1313+1258+693$ a''
27867	0	0	0.5	$1258+235^1$ a''	29665	0.6	0.3	0	$2\times1313+693$ a''

† The vibrational modes are designated a' or a'' of C_s symmetry, according to their symmetry with respect to the plane containing the CHO group and the aromatic ring.

TABLE 2 Vibrational Analysis and Relative Intensities Parallel to the a, b and c' axes for 2,4,5-trimethylbenzaldehyde$_{d-12}$ in durene$_{h-14}$, in absorption.

Frequency (cm^{-1})	Rel. Int. a	b	c'	Assignment	Frequency (cm^{-1})	Rel. Int. a	b	c'	Assignment
26413	4.8	0.4	0.3	0	27709	2.4	0.4	0	1296 a'
26434	1.3	0	1.4	0^1	27734	0.3	0.3	1.0	1296^1 a'
26617	0.6	1.8	0.9	204 a''	27787	0.6	0.5	0	1374
26639	0.6	0.7	0.8	204^1 a''	27915	0	1.0	0.7	1296 + 204 a''
26797	0.2	0.2	0	384	28140	0.2	0.5	0.9	1296 + 436
26850	0.8	1.0	1.4	437	28306	0.5	0.5	0.3	1296 + 595
26867	0	0	0.7	437^1	28413	1.0	0.8	1.1	1296 + 702 a''
27008	0.7	0.6	0	595	28789	0.3	0	0	1296 + 1081
27030	0.2	0.2	0	595^1	28829	0.5	0	0	1296 + 1122
27115	1.2	1.2	1.4	702 a''	28876	0.6	0	0	1296 + 1168
27137	0.3	0.4	0.4	702^1 a''	28995	1.0	0	0	2×1296 a'
27274	0.3	0.4	0.3	861	29021	0	0	0.4	2×1296^1 a'
27418	0.5	0	0	1005	29078	0.2	0.5	0.3	1296 + 1374
27494	0.6	0	0.6	1081	29419	0	0	0.3	$2 \times 1296 + 436$
27535	0.7	0	0	1122	29699	0	0.3	0.3	$2 \times 1296 + 702$ a''
27581	0.8	0	0	1168					

TABLE 3 The Excited Singlet States of 2,4,5-trimethylbenzaldehyde in n-hexane at 22 °C

Wavelength (Å)	Transition†	Extinction coefficient	Oscillator strength
3400	$\pi^* - n$	41	2×10^{-4}
2960	^1L_b	2010	1.2×10^{-2}
2570	C.T. + ^1L_a	17000	8.1×10^{-2}
2490	C.T. + ^1L_a	14450	

† Designation of transitions according to Shimada and Goodman.[2]

phosphorescence spectra of the protonated (ab) and deuterated (bc') aldehyde at 4 °K are shown in Figs. 4 and 5. In durene$_{d-14}$ both spectra are shifted by approximately 20 cm^{-1} to the blue. They should be compared with the phosphorescence spectrum of benzaldehyde[2] for which up to 4 quanta of the carbonyl stretching mode can be readily identified. A large number of ground state vibrations are observed such as 579, 707, 742 and 904 cm^{-1} (d-12 525, 610, 695 and 731 cm^{-1}), some perhaps involved in vibronic coupling because

of their different polarization. Low frequency modes are observed at 117, 167 and 204 cm^{-1} (*d*-12, 104, 138 and 194 cm^{-1}), but not one has the same intensity associated with it as the low frequency vibration in the absorption spectrum. By analogy with benzaldehyde,[18] the 204 cm^{-1} (*d*-12 194 cm^{-1}) vibration can be assigned to the out-of-plane motion of the —CHO as a whole and the 117 cm^{-1} (*d*-12 104 cm^{-1}) frequency to a —CHO torsion.

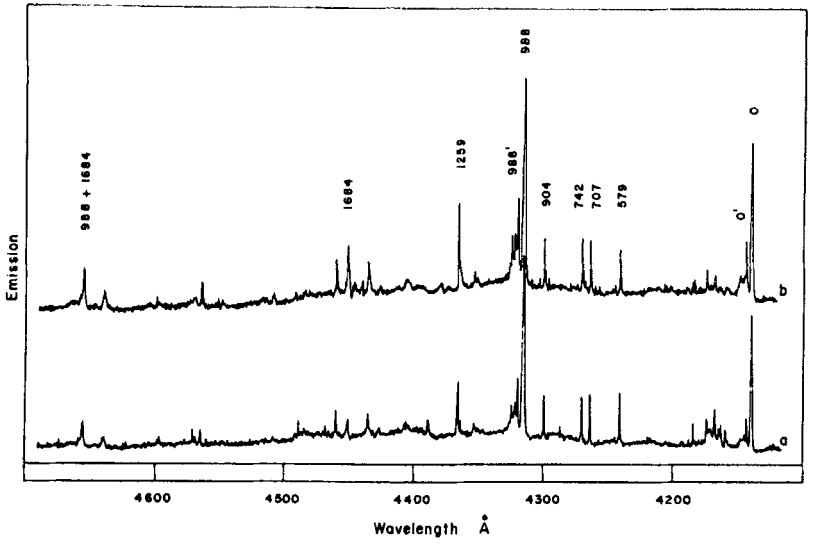

Figure 4. The phosphorescence spectrum of 2,4,5-trimethylbenzaldehyde$_{h-12}$ in durene$_{h-14}$ parallel to the *a* and *b* axes at 4 °K.

As for the absorption spectrum, most bands appear as doublets with the high frequency component the more intense and with frequency separation of 23 cm^{-1} (*d*-12 19 cm^{-1}). This is illustrated in Figs. 4 and 5. Lists of the more intense observed bands, their relative intensities and polarizations are contained in Tables 4 and 5. At 77 °K the band doubling is no longer evident. The vibrational structure is unchanged but band widths of 50 cm^{-1} are obtained.

The 0–0 band appears with approximately equal intensities along all three crystal axes. Despite the non-totally symmetrical nature of the C—H wagging mode at 988 cm^{-1} for a planar molecule, its apparent polarization is not very different to that of the 0–0 band.

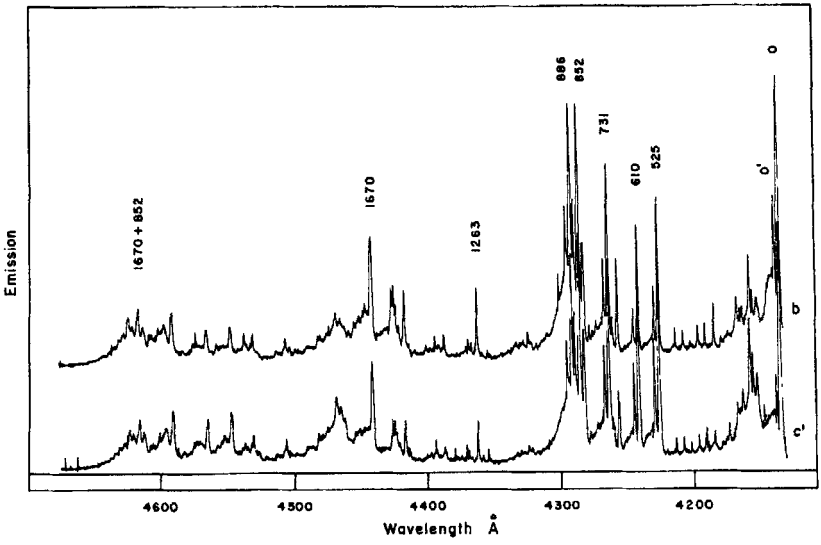

Figure 5. The phosphorescence spectrum of 2,4,5-trimethylbenzaldehyde$_{d-12}$ in durene$_{h-14}$ parallel to the b and c' axes at 4 °K.

TABLE 4 Phosphorescence Vibrational Analysis and Relative Intensities Parallel to the a, b and c' axes for 2,4,5-trimethylbenzaldehyde$_{h-12}$ in durene$_{h-12}$

Frequency (cm^{-1})	Rel. Int. a	b	c'	Assignment	Frequency (cm^{-1})	Rel. Int. a	b	c'	Assignment
24147	12.7	16.0	12.5	0	23108	1.4	1.7	0.8	1039
24124	3.7	3.0	2.2	0^1	23086	0.3	0	0.3	1039^1
24030	1.5	1.0	2.1	117 a''	22888	4.3	4.3	2.6	1259
24008	0.7	0.7	1.2	117^1 a''	22866	0.2	0.2	0.1	1259^1
23980	2.5	1.7	2.9	167	22537	1.3	1.8	0.9	1610
23943	1.7	1.9	1.1	204 a''	22463	2.5	2.9	2.8	1684 a'
23568	4.6	5.4	7.0	579	22415	2.0	2.0	1.6	(988 + 742)
23546	0.9	1.0	2.5	579^1	22391	0.4	0.4	0.4	(988 + 742^1)
23440	4.7	4.7	6.8	707	22343	0.3	0	0.5	1684 + 117 a''
23415	0.5	0.6	1.2	707^1	22290	0.4	0	0.4	1684 + 167
23405	4.6	4.6	2.7	742	22256	0.3	0.4	0.4	1684 + 204 a''
23380	0.5	0.4	0.2	742^1	21899	1.2	1.3	0.8	1259 + 988 a''
23271	0.2	0.2	1.2	876	21886	0	0	0.5	1684 + 579
23243	4.2	4.5	5.1	904	21750	0.3	0.3	0.4	1684 + 707
23222	0.6	0.7	1.1	904^1	21713	0.2	0.2	0	1684 + 742
23159	14.7	15.9	15.4	988 a''	21547	0.8	1.1	0.8	
23135	5.3	6.3	5.3	988^1 a''	21473	1.7	2.3	1.7	1684 + 988 a''

TABLE 5 Phosphorescence Vibrational Analysis and Relative Intensities Parallel to the a, b and c' axes for 2,4,5-trimethylbenzaldehyde$_{d-12}$ in durene$_{h-14}$

Frequency (cm^{-1})	Rel. Int. a	b	c'	Assignment	Frequency (cm^{-1})	Rel. Int. a	b	c'	Assignment
24189	15.8	16.8	15.4	0	23354	3.2	3.2	4.0	835
24170	5.2	4.5	4.9	0^1	23337	9.0	9.2	9.1	852 a''
24085	0.8	1.0	1.2	104 a''	23316	2.8	2.8	3.3	852^1 a''
24066	1.9	1.1	1.2	(104^1) a''	23303	6.9	7.0	6.2	886
24051	3.5	2.5	3.0	138	23283	2.7	2.7	2.5	886^1
24021	1.2	0.8	1.0	(168)	23131	0.9	0.7	0.4	1058
24010	0.4	0.6	0.7	(179)	22926	2.9	2.8	2.0	1263
23995	1.2	1.0	1.3	194 a''	22904	0.2	0.4	0.2	1263^1
23900	1.4	1.2	2.4	289	22642	3.2	3.0	1.8	1547
23864	0.9	1.0	1.4	(325)	22620	0.6	0.6	0.4	1547^1
23832	0.7	0.9	1.1	357	22519	3.6	4.2	3.7	1670 a'
23799	0.3	0.3	0.5	(390)	22416	0.1	0.1	0.3	1670 + 104 a''
23768	0.7	0.7	0.9	421	22398	0.4	0.4	0.6	1670 + (104^1) a''
23734	0.6	0.7	1.1	456	22380	0.7	0.7	1.1	1670 + 139
23664	4.5	4.6	6.9	525	22349	0.2	0.2	0.3	1670 + 168
23645	1.7	1.8	2.6	525^1					
23579	4.1	4.1	5.9	610	21988	1.2	1.2	1.4	1670 + 525
23561	1.2	1.2	1.7	610^1	21907	1.2	1.2	1.4	1670 + 610
23494	3.5	2.6	4.0	695	21780	1.7	1.7	1.8	1670 + 731
23473	1.0	0.8	0.8	695^1	21660	1.9	1.7	1.2	1670 + 852
23458	7.3	7.5	9.0	731	21623	1.2	0.8	8.8	1670 + 886
23438	2.6	2.9	4.2	731^1					

4. Discussion

SITE SPLITTING AND TRANSITION POLARIZATIONS

The assignment of the absorption spectrum to an $\pi^* \leftarrow n$ transition is consistent with the observed vibrational structure and with the similarly assigned transitions of related compounds. But it is inconsistent with the transition polarization expected for a planar molecule oriented with its molecular axes parallel to those of durene in a durene crystal. The 0–0 band in the absorption spectrum is polarized almost parallel to the a crystal axis (Figs. 2 and 3 and Table 6b). For an $\pi^* \leftarrow n$ transition, the electronic transition moment is parallel to the molecular normal, x. Thus for a durene

crystal the 0–0 band should appear with approximately equal intensities along the a and b axes and with much less intensity parallel to the c' axis (Table 6a). The following explanations are proposed for this lack of agreement.

Intermolecular host-guest interactions can significantly alter polarization ratios from the ideal, oriented-gas values.[21] The modified polarization ratios, determined by second-order perturbation theory[22] and based only on dipole-dipole interactions are listed in Table 6c. As such they do not provide a satisfactory explanation. However, as for resonance interactions, the inclusion of higher and permanent moments into the calculation may lead to a result more in agreement with experiment.[21]

On the other hand the unexpected polarization may result from a changed orientation of the trimethylbenzaldehyde in the durene crystal. An orientation in which the aldehyde group or the whole molecule is rotated, mainly about c', so that the normal, x, is now approximately parallel to a will lead to the observed polarization of the 0–0 band in absorption.

Most bands of the absorption and emission spectra appear as doublets. The doublet splitting differs for absorption and emission and differs for the fully protonated and deuterated forms of the aldehyde. It is independent of the host insofar as its extent of deuteration is concerned. The most reasonable explanation relates this band doubling to the two crystallographically inequivalent aldehydes that exist in the durene crystal. The other probable interpretation involves the activity of a low frequency lattice vibration. However, the narrow and similar bandwidths of the doublet components, the intensities and the differing polarization behavior as distinct from what is believed to be obtained for genuine phonon structure, including the lattice vibrations observed at higher frequencies, all favour the former interpretation. This is particularly evident in the emission spectra where apart from the band doubling very little intensity is associated with phonons. The difference in the total intensity of the two components, for the 0–0 band approximately a factor of 2 (Tables 1 and 2 and Figs. 2 and 3), in the absorption spectrum may arise from the greater stability of one configuration. This is not unreasonable since the two crystal configurations are physically different and experience different intermolecular

TABLE 6A The Oriented-gas Polarization Ratios for the Systems of Axes Depicted in Fig. 1. For the xyz system there are two sets of polarization ratios, I and II, corresponding to the two crystallographically inequivalent configurations. For the $x'y'z'$ system the polarization ratios are the same for the two configurations provided the C = 0 axis is parallel to z'.

	I			II						
	b/a	b/c'	a/c'	b/a	b/c'	a/c'		b/a	b/c'	a/c'
x	0.785	77.7	98.9	0.785	77.7	98.9	x'	0.785	77.7	98.9
y	0.874	0.298	0.341	2.300	0.195	0.085	y'	1.311	59.8	45.6
z	1.621	0.986	0.608	1.090	1.944	1.784	z'	0.032	0.0005	0.014

TABLE 6B The Experimentally Observed Polarization Ratios

Band type	Absorption b/a	b/c'	a/c'	Band type	Phosphorescence b/a	b/c'	a/c'
0	0.04	0.4	10.3	0	1.2	1.2	1.0
a'				a'			
0′	0.00	0.00	1.7	0′	0.8	1.4	1.7
235	1.5	1.6	1.1	988	1.1	1.0	0.95
a''				a''			
235′	0.8	0.45	0.55	988′	1.2	1.2	1.0

TABLE 6C The Mixed Crystal Polarization Ratios for an Out-of-Plane Polarized Transition Modified by Intermolecular Interactions and Calculated on the Basis of Dipole-dipole Interactions only[23]

	b/a	b/c'	a/c'
x	0.796	46.7	58.6

interactions. It requires that at some stage in the process of obtaining the mixed crystal at 4 °K from the melt a Boltzmann process is operative.

Provided that the interpretation of the doublet structure is correct the different polarization behavior of the doublet components, in particular as demonstrated for the 0–0 band of the absorption spectrum, requires the participation of intermolecular interactions or changes in guest orientation or loss of molecular planarity or some combination of the three.

ESR studies of the triplet state[13] predict a mixed crystal structure in which the CHO group is coplanar with the aromatic ring and $x'y'z'$ of the guest parallel to xyz of the durene. This implies that at least for the triplet state if not also the singlet, intermolecular interactions are responsible for modifying the polarization ratios from those expected for an oriented gas.

The optical properties of a durene crystal correspond to a pseudo-orthorhombic crystal,[24] that is, the principal axes of the indicatrix are exactly parallel to the b and approximately parallel to the a and c' crystal axes. Thus the real orientation of the polarized radiation in passing through the crystal corresponds to that of the incident radiation, and no error is introduced into the predicted polarization ratios as a result of a changed orientation of the radiation in the crystal.

Phosphorescence Assignment

The assignment of the phosphorescence spectrum is ambiguous since features present in the spectrum are characteristic of both $\pi^* \rightarrow \pi$ and $\pi^* \rightarrow n$ transitions. The occurrence of a large number of ground state vibrations and the lack of a strong progression in the carbonyl stretching mode, contrary to the results for benzaldehyde, are features representative of the former designation. On the other hand, the very large zero-field splitting parameter, $D/hc = \pm 0{\cdot}335$ cm^{-1} and the short phosphorescence lifetime, 33×10^{-3} secs relative to the $^3\pi\pi^*$ phosphorescence of 2-naphthaldehyde,[8] 0·4 secs in EPA at 77 °K (benzaldehyde[25] 1.2×10^{-3} secs in EPA at 77 °K) provide strong evidence of the localized nature of the transition, indicative of a $^3n\pi^*$ state.

Further evidence of the $3n\pi^*$ nature is provided by the deuteration shift tabulated in Table 7. This shift is approximately 1/5th that

TABLE 7 Deuteration Shifts in the Absorption and Phosphorescence Spectra of Benzaldehyde, 2,4,5-trimethylbenzaldehyde and Durene, (cm^{-1}).

	Benzaldehyde[17]			Trimethyl-benzaldehyde†			Durene		
	D_0	D_6	Δ	D_0	D_{12}	Δ	D_0	D_{14}	Δ
Absorption	26916	26972	56	26350	26413	63	35554	35690‡	136
				26350	26411	61			
Phosphorescence				24147	24189	42	28000	28180[11]	180
				24166	24206	40			

† In durene$_{h-14}$ and durene$_{d-14}$. ‡ The author's unpublished results.

observed for the ($\pi\pi^*$) phosphorescence of durene. Furthermore, it is comparable to that obtained in absorption and also to that in the absorption of benzaldehyde, both involving $^1n\pi^*$ states. The small deuteration shift is consistent with a localized transition in which only the aldehyde group has experienced a marked change in configuration.

Predictions on the polarization of the phosphorescence can be made from considerations of the spin-orbit coupling mechanisms responsible for giving the singlet-triplet transition dipole strength. For the limiting case of a planar molecule and with the approximation that the carbonyl group is the major perturbation on the aromatic ring, an instructive treatment of the important matrix elements can be carried out under C_{2v} symmetry.

For a $^3n\pi^*$ state it is expected[26] that most of the intensity is introduced via the direct mechanism, involving the out-of-plane spin-orbit operator. The matrix element is

$$\frac{\langle {}^3A_2(^3n\pi^*) \mid H_{s.o.}^{(C2)} \mid {}^1A_1(^1\pi\pi^*)\rangle}{E_{^1A_1} - E_{^3A_2}}$$

This leads to polarization parallel to the C_2 axis.

Spin-orbit, vibronic mechanisms may also be responsible for some of the intensity. For benzophenone,[5] $^3n\pi^*$ in the C_{2v} model, it has been determined that apart from the direct mechanism described above a second-order mechanism is also active.

$$\frac{\langle {}^3A_2(^3n\pi^*) \mid H_{s.o.}^{(x)} \mid {}^1B_1(^1\sigma\pi^*)\rangle\langle {}^1B_1(^1\sigma\pi^*) \mid H_\nu(a_2) \mid {}^1B_2(^1\pi\pi^*)\rangle}{(E_{^1B_1} - E_{^3A}) (E_{^1B_2} - E_{^3})}$$

This results in in-plane polarization perpendicular to the C_2 axis. Spin-orbit coupling with the $^1B_1$ state is very large, but transitions to this state are weak and hence vibronic coupling with the $^1B_2$ state can compete. H_ν is the first derivative of the electronic Hamiltonian with respect to the displacements a_2 (in C_s symmetry a''). Direct spin-orbit coupling with the $^1B_2$ state is weak and hence its contribution is small. For this second-order mechanism to be of comparable importance to the direct one above, (*a*) the matrix element

$$\langle {}^3A_2({}^3n\pi^*) \mid H_{s.o.}^{(x)} \mid {}^1B_1({}^1\sigma\pi^*)\rangle$$

must be considerably larger than

$$\langle {}^3A_2({}^3n\pi^*) \mid H_{s.o.}^{(C2)} \mid {}^1A_1({}^1\pi\pi^*)\rangle$$

and (*b*) the $^1B_2$ state vibronically coupled is not the one at 34000 cm^{-1}, in *n*-hexane, but a higher one for which the oscillator strength for absorption is much larger, such as the ^1B_b state. This is a result of the very large denominator term in the second-order expression.

In the reduced symmetry C_s, more applicable to this molecule, both mechanisms predict in-plane polarized phosphorescence. The 0–0 band should be polarized parallel to the approximate C_2 axis and those bands involved in vibronic coupling (a'' modes) should appear with greater intensity perpendicular to the approximate C_2 axis. The observed polarization ratios and those predicted for the ideal mixed crystal are tabulated in Tables 6a and 6b. It is seen that neither for the *xyz* or *x'y'z'* system of axes is the agreement good, although it is better for the *xyz* system of axes.

Chakrabarti[27] has recently discussed the spin-orbit coupling mechanisms for a $^3\pi\pi^*$ state in relation to the phosphorescence of 2-naphthaldehyde. Both the direct and spin-orbit vibronic mechanisms are believed active. However, for the origin band, only the direct mechanism applies leading to *x* polarized phosphorescence. In durene out-of-plane polarized transitions should appear with low intensity parallel to the *c'* axis. Thus the observation of considerable phosphorescence intensity of the 0–0 band along *c'* favours the $^3n\pi^*$ assignment.

Hirota[1] believes that the magnitude of the zero-field splitting and the directions of the principal axes may be more reliable guides to the $^3\pi\pi^*$ or $^3n\pi^*$ character of an emitting state than other criteria

previously mentioned, on the grounds that they appear less sensitive to the mixing of both states. However, the results for benzophenone[28,29] whose lowest triplet state is $^3n\pi^*$ with $D/hc = -0.15$ cm^{-1} (formaldehyde $^3n\pi^*$ $D/hc = +0.42$), cast doubt on the validity of employing the magnitude of the zero-field splitting as a sole criterion of the nature of the emitting state.

For 2,4,5-trimethylbenzaldehyde most of the evidence clearly supports the $^3n\pi^*$ assignment as for benzaldehyde itself. However the substitution of methyl groups in benzaldehyde, in particular para methyl, has considerably modified the vibrational envelope of the emission. Tetramethylpyrazine[30] has a lowest $^3\pi\pi^*$ level whereas pyrazine has a $^3n\pi^*$ level lowest. Similarly for para-substituted benzaldehydes it has been observed[31] that the chloro- and bromo-derivatives have emission characteristics typical of a $^3n\pi^*$ state while for the hydroxyl and amino derivatives the emission, insofar as the vibrational envelope and lifetime are concerned, is characteristic of a $^3\pi\pi^*$ state.

The origin of the shift, recorded in Table 7, in the phosphorescence spectrum, but not in the absorption spectrum, upon deuteration of the durene host is puzzling. A similar mixed crystal, phenanthrene in biphenyl, also showing site splitting has no observable shift in its phosphorescence spectrum upon deuteration of the biphenyl. The shift is independent of the aldehyde concentration. A crystal containing both the *h*-12 and *d*-12 aldehydes in durene, in approximately equal concentrations gave spectra identical with the spectra of the individual aldehydes. Thus no microcrystallite formation occurred. The occurrence of intermolecular hydrogen bonding involving the carbonyl oxygen, may be the cause of the shift. Further work along these lines is being carried out.

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