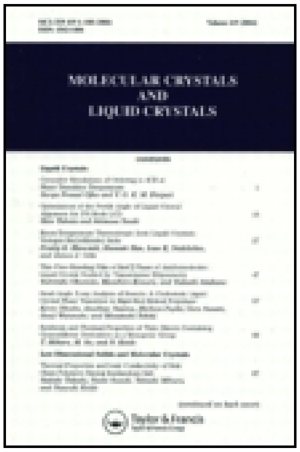

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The 3000 Å Absorption Spectrum of Phenanthrene in Mixed Crystals

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The 3000 Å Absorption Spectrum of Phenanthrene in Mixed Crystals

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Abstract—The polarized second singlet–singlet absorption spectrum of phenanthrene at 3000 Å has been observed in mixed crystals of durene and hexamethylbenzene. In durene at 4 °K, bandwidths of 10 cm^{-1} are observed and lattice vibrations identified. Electron spin resonance measurements of the phenanthrene triplet in durene have shown that the orientation of the phenanthrene is changed from that of the durene. Nevertheless the observed polarization ratios are close to those calculated for a long-axis polarized mixed crystal transition. All the results are in agreement with the assignment of $^1B_2$ for the second singlet state.

Introduction

Phenanthrene, in common with a number of other aromatic hydrocarbons, has three absorption systems in the wavelength range 3500 to 2500 Å. The first one at 3400 Å, which is short-axis polarized, has been studied in detail in pure crystals[1,2,3], mixed crystals[1,4] and in low temperature glasses.[5]

On the other hand the second singlet–singlet system at 3000 Å has received comparatively little attention. It has been studied in solution of *n*-pentane at − 100 °C[5] and also in the pure crystal.[6] From the crystal work it is concluded that, despite the poor agreement between the calculated and experimentally measured Davydov splitting and polarization ratios, the absorption at 3000 Å is long axis polarized. In the pure crystal it is believed that the absorption intensities of the 3000 Å system include some contribution from the intense 2500 Å system, apparently resulting from the Davydov splitting. This problem is not encountered in mixed crystals. Nevertheless even in mixed crystals the polarization ratios differ from the oriented gas ones because of crystal field mixing of the guest and host transitions.[7]

The host crystals durene and hexamethylbenzene are transparent in the region of the 3000 Å absorption of phenanthrene and form mixed crystals, although dilute, in which the phenanthrene is not randomly oriented. Furthermore these mixed crystals are of particular interest because they represent systems in which the large differences in molecular dimensions of host and guest molecules may be expected to lead to local distortions of the host crystal structure and to changes in the orientation of the guest within the host lattice. The possibility of the phenanthrene occupying more than two sites in the unit cell may also arise as for quinoline in durene.[8]

A satisfactory interpretation of the polarization ratios depends on a knowledge of the guest orientation and of the host–guest interaction. This interaction, itself depends on the relative orientations. The extent of the host–guest interaction can be estimated from the expressions deduced by Craig and Thirunamachandran[9] appropriate to the case of the deep trap limit. The transition moment to the upper state of the guest in the mixed crystal is given by

$$M = c^{-1/2}\left[M^{r}_{1m} + \frac{\left(M^{s}_{a}\sum_{i(a)}' H_{i(a)p} + M^{s}_{b}\sum_{i(b)}' H_{i(b)p} + \cdots\right)}{\Delta w^{r}_{G} - \Delta w^{s}_{H}}\right] \tag{1}$$

where M^{r}_{1m}, M^{s}_{a} and M^{s}_{b} are transition moments of host and guest, taken from solution work, $\sum_{i(a)}' H_{i(a)p}$ and $\sum_{i(b)}' H_{i(b)p}$ are lattice sums, $\Delta w^{r}_{G} - \Delta w^{s}_{H}$ is the difference in transition energy and c is a normalizing constant.

By means of paramagnetic resonance spectroscopy of the phenanthrene when excited into its lowest triplet state the orientation of the molecular axes relative to the crystallographic axes can be determined. The principal axes are assumed parallel to the molecular axes. In aromatic molecules the dipolar electron spin–spin interaction is primarily responsible for removing the degeneracy of the triplet state. In the presence of an external magnetic field the Hamiltonian describing the splitting of the triplet state is given by

$$H = g\beta H \cdot S + D(S_z^2 - 1/3S^2) + E(S_x^2 - S_y^2) \qquad (3)$$

The zero field splitting parameters D and E for phenanthrene have been previously measured from work on mixed crystals with fluorene and biphenyl.[10]

Experimental

The absorption spectra were recorded on Eastman-Kodak 103–0 film in the second order of a 1.5 m Bausch and Lomb spectrograph with dispersion 7.5 Å per mm and at higher resolution on Ilford R30 plates in the first order of a 3.4 m Jarrell–Ash spectrograph with dispersion 2.4 Å per mm. The lines of an iron hollow-cathode lamp served as calibration and wavelengths could be measured to within 1 cm^{-1}. The optical density ratios were obtained from microdensitometer tracings recorded with a Joyce–Loebl. Where the optical density ratios are approximately 1 and the actual optical densities in the range 0.1 to 2 the errors in determining the ratios are small, within 10%. The polarization ratios are taken equal to the optical density ratios. A Wollaston prism served to separate the transmitted light into two perpendicular polarizations.

The durene (Fluka purum) was sublimed and zone refined in vacuo for more than 50 passes and at the conclusion of the purification process showed no evidence of its characteristic aldehyde impurity.[11] The phenanthrene (Fluka puriss) and the perdeutero phenanthrene (Merck, Sharp and Dohme) were both zone refined, the phenanthrene being first treated with maleic anhydride to effect removal of anthracene impurity. The hexamethylbenzene (Eastman Organic Chemicals) was also zone refined. The methylcyclohexane (Matheson Coleman and Bell, spectroscopic reagent) was used as such. Naphthalene (Fluka, puriss) was treated with potassium and zone refined and sublimed.

The mixed crystals were grown from the melt. Crystal specimens with the *ab*, *bc′* and *ac′* faces developed were obtained by standard techniques. Crystals in the range of thicknesses 1 to 5 mm were used. The phenanthrene concentrations were estimated from the absorption intensities and an upper limit of 10^{-4} mole fraction was imposed by the absorption intensity of the first singlet system.

A metal cryostat (hofman) in which the sample is attached to a cold finger was employed in the measurement of the polarization ratios and a glass cryostat in which the sample is immersed in the liquid helium was otherwise employed.

The magnetic resonance measurements were recorded with a Varian V4502–15 EPR spectrometer. The measurements were made on crystals of phenanthrene in durene of approximately 2×10^{-5} mole fraction at $-180\,°C$ and at 9.233 cps. The crystals were approximately 2 mm cube and were continuously irradiated with a 200 watt high pressure mercury/xenon arc (Hanovia), with the external magnetic field in the *ab*, *bc′* and *ac′* planes. The magnetic resonance spectra, for the field in the *ab* plane, were repeated for a number of different crystals and closely reproducible results obtained.

Results

The second singlet–singlet absorption spectrum of phenanthrene in methylcyclohexane at 77 °K is shown in Fig. 1. The spectrum is very similar to that of phenanthrene in N-pentane at $-100\,°C$[5]. The bands are broad, band width 200 cm^{-1}, and the spectrum of the perdeutero phenanthrene is shifted 70 cm^{-1} to the blue. The polarized spectra with incident light normal to the *ab* and *bc′* faces of mixed crystals of $\text{phenanthrene}_{h-10}$ and $\text{phenanthrene}_{d-10}$

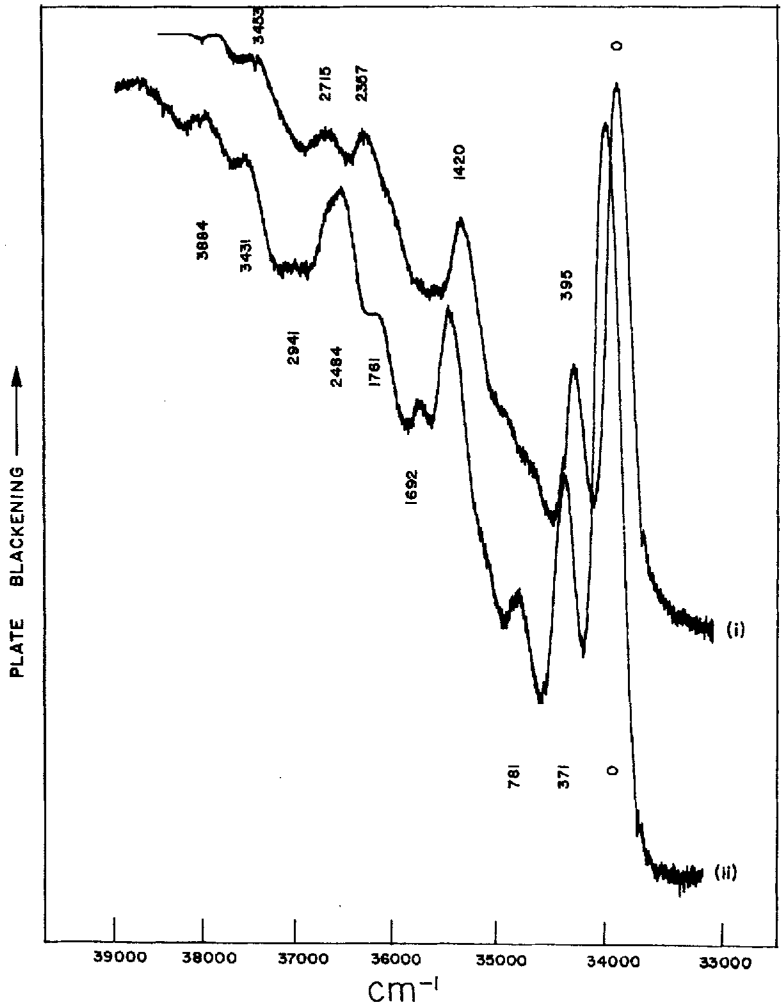

Figure 1. The second singlet absorption system of (i) phenanthrene$_{h-10}$ and phenanthrene$_{d-10}$ in methylcyclohexane at 77 °K.

in durene at 4 and 77 °K are shown in Figs. 2, 3 and 4. The absorption appears with greatest intensity parallel to the *a* and *b* axes.

The durene crystal spectra are displaced some 450 cm^{-1} to the red but are otherwise little changed relative to the methylcyclohexane frozen glass spectra, and both are similar to the pure crystal spectrum reported.[6] Both in the mixed crystal and in the

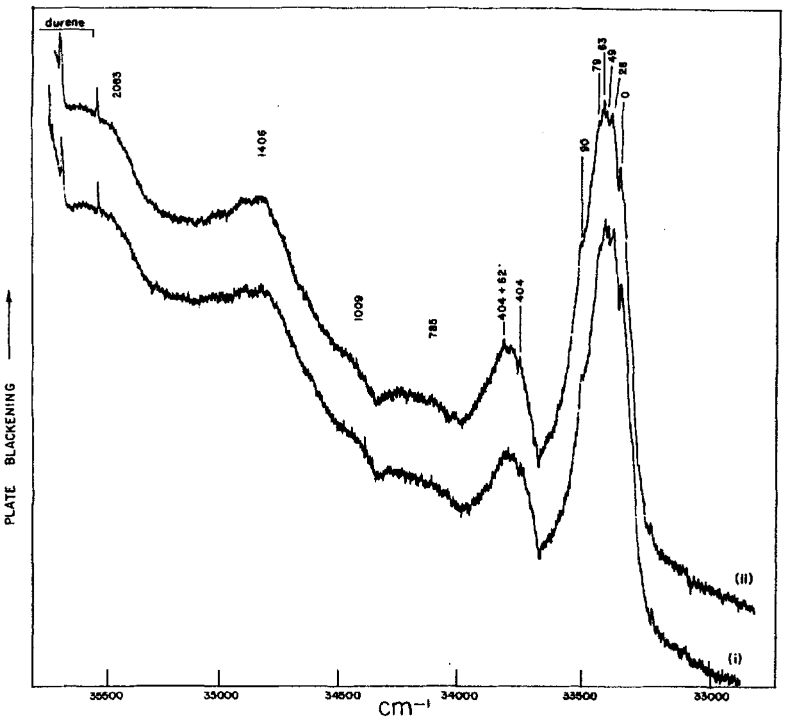

Figure 2. The (i) *a* polarized and (ii) *b* polarized second singlet absorption system of phenanthrene$_{h-10}$ in durene at 4 °K. The spectrum was recorded with the glass dewar where a degree of depolarization occurs and consequently the curves labelled *a* and *b* contain some admixture of opposite polarization. The lattice structure is clearly marked in the intense origin band. The narrow line-like bands at the onset of the durene absorption, unrelated to the presence of the phenanthrene, are also clearly marked.

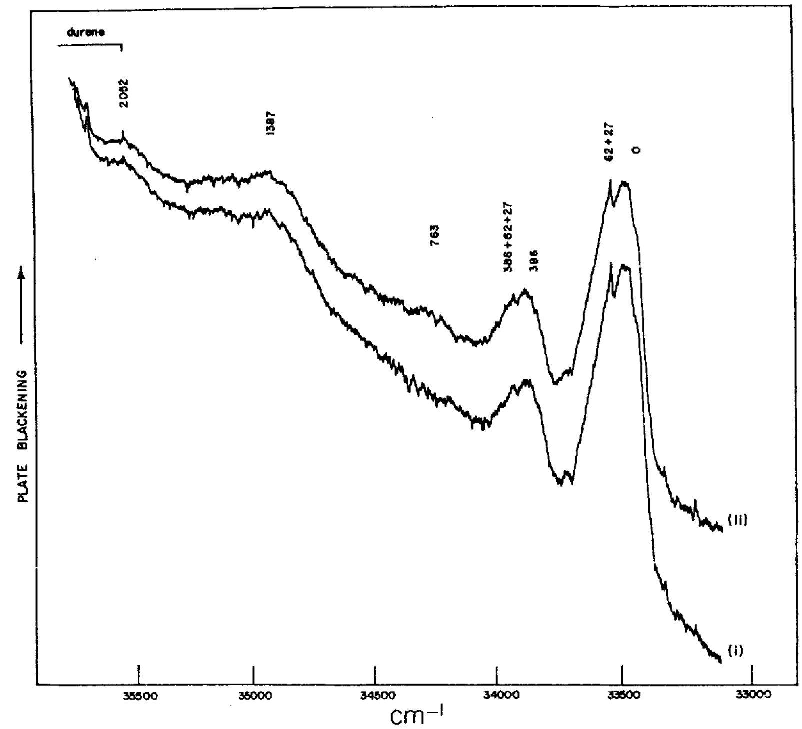

Figure 3. The (i) *b* and (ii) *a* polarized second singlet absorption spectrum of phenanthrene$_{d-10}$ in durene at 4 °K. Again the lattice structure is clearly evident.

frozen glass the broad origin band corresponding to the first band in the spectrum is the most intense. Vibrational analyses of the mixed crystal and frozen glass spectra are presented in Tables 1 and 2. Because of the host crystal absorption the mixed crystal spectra can only be observed for about 2300 cm^{-1}.

With the incident light normal to the *ab* face of hexamethylbenzene, the phenanthrene absorption also appeared polarized, but in this case the absorption at 130 °K consisted of a single broad band at 33424 cm^{-1}, phenanthrene$_{d-10}$ 33484. The different solid phases of this host make absorption studies at much reduced temperatures difficult.

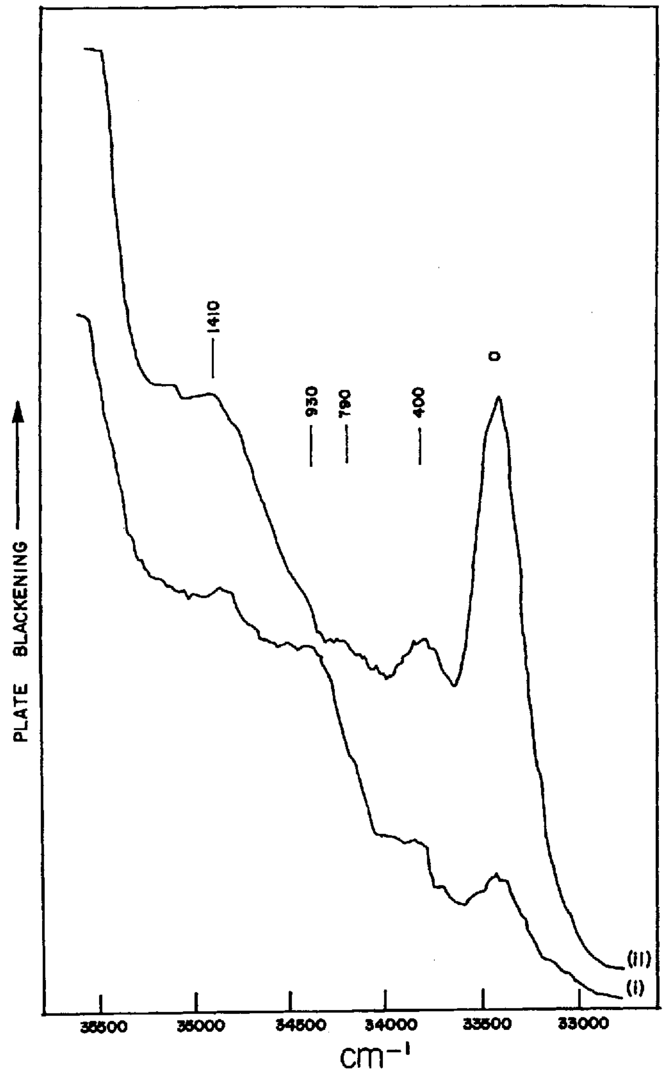

Figure 4. The (i) *c*' and (ii) *b* polarized second singlet absorption of phenanthrene$_{h-10}$ in durene at 77 °K. Lattice structure is not resolved at this temperature.

TABLE 1 Vibrational analysis of the second singlet system of phenanthrene$_{h-10}$

Durene				Methylcyclohexane		Pure Crystal[a]
(4 °K)				(77 °K)		(4 °K)
ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	Rel.[c] Int.	analysis	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\Delta\nu$ (cm^{-1})
33294	−65	vw(sh).				
33321	−35	vw(sh).				
33359	0	vs	0	33577	0	0
33387	28	vs	27			
33408	49	vs	49, 2 × 27			
33422[b]	63	vs	62			
33438	79	vs	49 + 27			
33449	90	s(sh).	62 + 27			
33511	152	s	151, 2 × 62 + 27			
33763	404	m	404 a_1[d]	34272	395	400
33797	438	m	404 + 27			
33816	457	m	404 + 2 × 27			
33828	469	m	404 + 62			
33853	494	m(sh.)	404 + 62 + 27			
34207[b]	785	w	785, 2 × 404	34652	775	
34354[b]	932	w(c')[e]	932 b_2			
34431[b]	1009	vw	1009 a_1	34882	1005	975
34768[b]	1346	vw(c')	932 + 404			
34828[b]	1406	m	1406 a_1	35300	1423	1465
35425[b]	2003	vw(c')		35589	1712	
35505[b]	2083	m				
35653[b]	2231	vw(c')		36234	2357	
				36592	2715	
				37330	3453	
				37753	3876	

NOTES: [a] Results of Gordon[6].

[b] For the bands of low intensity only the frequencies of the band maxima are given. $\Delta\nu$ for these bands refer to separations of band maxima.

[c] Relative intensities designated vw, w, m, s and vs, very weak, weak medium, strong, very strong, respectively. Bands appearing as shoulders, sh.

[d] Assignment of excited state fundamentals, a_1 and b_2 of C_{2v} symmetry.

[e] Intensity only parallel to c'.

TABLE 2 Vibrational analysis of the second singlet system of phenanthrene$_{d-10}$.

	Durene (4 °K)				Methylcyclohexane (77 °K)		Pure Crystal (4 °K)
ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	Rel. Int.	analysis	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\Delta\nu$ (cm^{-1})
33357	−55	w				
33403	−39	w				
33442	0	vs	0	33948	0	0
33463	21	vs				
33471	29	vs(sh.)	27			
33482	40	vs(sh.)				
33495^b	53	vs	2×27			
33534	92	vs	$62 + 27$			
33561	119	vs(sh.)	2×62			
33828	386	m	386 a_1	34319	371	400
33851	409	m	$386 + 27$			
33874	432	m	$386 + 2 \times 27$			
33921	479	m	$386 + 62 + 27$ . .			
34258^b	763	w	763, 2×386	34729	781	815
				35028	1080	
34882^b	1387	m	1387 a_1	35375	1427	1450
				35640	1692	
35546^b	2051	m		35909	1961	1830
				36432	2484	
				36889	2941	
				37379	3431	
				37832	3884	

The broad band envelopes in the durene mixed crystal spectra, evident at 77 °K, are resolved into a number of much narrower bands, of about 10 cm^{-1} band width. This resolvable structure is not limited to the origin band but appears in a very similar form in other bands in the spectrum and is particularly noticeable in the second most intense band 400 cm^{-1} removed from the origin. It is independent of the particular crystal studied since it was observed for a number of different crystal specimens and also for phenanthrene$_{d-10}$. The almost exact repetition of the fine structure in the majority of bands in the spectrum indicates that the bulk of the fine structure does not derive from overlapping bands of the first singlet system. It is best explained as arising from the excitation of lattice vibrations. The presence of different sites could also be responsible although the EPR evidence presented does not favour this interpretation.

Lattice modes of 27, 49 (may be 2 × 27) and 62 cm^{-1} are detected. McClure[12] observed lattice modes of 15, 27 and 62 cm^{-1} in the absorption spectrum of naphthalene in durene.

The origins of the electronic transitions are tentatively assigned to the bands at 33359 and 33442 cm^{-1} for phenanthrene$_{h-10}$ and d–10 respectively. The selection of these bands as origins is consistent with the pattern of intensities observed and the isotopic shift is of the right magnitude. Some weak bands appearing as shoulders to the red of the origins, particularly for phenanthrene$_{d-10}$ may be due to isotopic impurities or overlapping bands of the first singlet system. They may also result from a small percentage of the guest molecules occupying other sites.

In view of some recent work on bandwidths of electronic spectra of aromatic molecules[13] it is of interest to note that in the second system of phenanthrene bandwidths as small as 10 cm^{-1} are obtained. Similar bandwidths have been obtained in the second system of naphthalene in the vapour.[14] Bandwidths of less than 2 cm^{-1} are obtained in the first system of phenanthrene.

The vibronic structure of the second absorption system is quite different to that of the 3400 Å system. This is manifested by the different distribution of intensity among the vibronic bands. Most of the intensity is in the broad origin band and in totally symmetric vibrations based on the origin. In distinction to the first singlet–singlet system, the totally symmetric bands, a_1 of C_{2v} symmetry point group, at 674 (h–10) and 629 (d–10) cm^{-1}, which vibronically couple the first singlet system with the intense one at 2500 Å and account for about half the intensity, are absent in this spectrum. If the second singlet state at 3000 Å is of symmetry B_2 then this is to be expected since now b_2 vibrations are required to bring about intensity stealing from the A_1 state at 2500 Å by vibronic coupling. The low intensity, c' polarized band at 932 (h-10) cm^{-1}, assigned as a b_2 fundamental, is such a band in question. However it plays only a minor role in the spectrum, not at all comparable with that of the 674 cm^{-1} mode in the spectrum of the first excited singlet state. This interpretation of the vibrational structure is in agreement with the explanations given for the anomalous intensity of the 674 cm^{-1} band in the first singlet system. It is also in agreement with the prediction of an A_1 electronic state at shorter wavelengths.

The a_1 fundamentals at 400 and 1410 cm^{-1}, characteristic bands of a large number of aromatic hydrocarbons, are prominent in the spectrum and are not greatly changed from their ground state values. The a and b polarized bands of medium intensity at 2083 and 2052 cm^{-1} for phenanthrene$_{h-10}$ and phenanthrene$_{d-10}$ are not readily assigned. Similar bands in the first system have been assigned as combination bands, 1409 + 674 and 1434 and 629 cm^{-1}. This assignment is not entirely satisfactory for the second system since no bands of observable intensity are obtained at 674 and 629 cm^{-1}. No assignment of the bands of phenanthrene$_{h-10}$ and phenanthrene$_{d-10}$ in methylcyclohexane, removed more than 2000 cm^{-1} from the origin is presented. It is felt that any analysis would be ambiguous and largely unsubstantiated since these are not combination bands of observed fundamentals. Nor are they expected to be pure fundamentals since the predominant modes in the electronic transitions of aromatic hydrocarbons are carbon–carbon in nature with frequencies less than 2000 cm^{-1}. Similarly the very weak c' polarized bands of phenanthrene$_{h-10}$ at 2003 and 2231 cm^{-1} have not been assigned. It is possible that these bands record the commencement of another electronic transition. The two transitions would be of comparable intensities. The polarization is not established since bands are observed parallel to both b and c'. For azulene in alcohol solution at 77 °K, a further electronic transition is observed, about 5000 cm^{-1} to the blue of the origin of the second system, on the steep absorption front of the fourth electronic transition.[15]

The polarization ratios of some of the prominent bands in the spectrum are listed in Table 3 together with the oriented gas ratios and the mixed crystal ratios based on expression (1). The lattice sums in equation (1) are taken as dipole–dipole sums and calculated over a sphere of radius 130 Å. The oscillator strengths are solution values[6,16] see appendix. Two cases are considered, one where the durene is assumed to possess intense ($f = 1$) L and M transitions at 1800 Å, and two where these are neglected. Best agreement is obtained for a transition which is polarized parallel to the molecular long axis. The calculated polarization ratios are based on the assumption that the guest molecule has adopted an orientation in the host lattice in which its molecular axes are parallel to those of the replaced host molecule. It is shown in the following section that this assumption is not entirely warranted.

TABLE 3 Polarization ratios for phenanthrene in durene

	Experiment		Theory				
				Oriented Gas		Mixed Crystal	
Band type	b/a	b/c'		L	M	L	M
0	1.2	5.4	b/a	1.3	0.032	1.76(1.37)[a]	0.0019(0.019)
400	1.2	4					
1400	1		b/c'	60	0.00045	62(58)	0.000024(0.00026)

[a] Values in parenthesis refer to exclusion of 1800 Å system of durene in calculations.

At 4 °K some very narrow absorption bands are observed at the onset of the durene host crystal absorption. These bands are polarized parallel to the a and b crystallographic axes and are unchanged in durene crystals and in mixed crystals with phenanthrene. Thus, although no immediate explanation is available for the origin of these bands, they are not caused by distortions of the host crystal structure resulting from the inclusion of some phenanthrene. They can be seen in Figures 2 and 3.

ESR Measurements

Durene is a monoclinic crystal with two molecules per unit cell.[17] Thus in general resonance is observed at four different field strengths for the $\Delta m \sim 1$ transitions. The variation of the field strength for resonance with rotation of the crystal about its c' axis, that is rotation of the field in the *ab* plane, is shown in Fig. 5. The measurements were conducted at $-180\,°\mathrm{C}$. Since no more than four signals are observed the phenanthrene occupies no more than two different sites. This is in accordance with the crystal structure of durene.

For durene the plane containing the long axis and the normal to the molecular plane of one molecule is almost coplanar with a similar plane of the other molecule in the unit cell and both are almost coplanar with the *ab* crystallographic plane. Assuming that the phenanthrene is substituted with its molecular axes parallel to the durene, then the stationary points in the curves of Fig. 5 correspond to the field lying parallel to the molecular axes. When the field is parallel to the *b* axis, the screw axis relating the two unit cell sites, the two sites are identical and two instead of four resonances are observed. This applies even if the guest has changed its orientation relative to the host and if the host has suffered local distortions in the neighbourhood of a guest. It is of course assumed that the principal axes of the zero field splitting tensor and the molecular axes are coincident.

In Fig 5, the field parallel to the *a* and *b* axes corresponds to 13 and 103° respectively, and the stationary points are displaced about these positions by ± 42 and ± 48°. In these measurements the error is less than ± 1°. This is in accord with the orientation of a durene molecule in a durene lattice, 41.4 and 48.6°, but does not on its own indicate that the molecular axes are in the *ab* plane and parallel to the field at these orientations.

On the other hand making the assumptions that the phenanthrene is substituted with its molecular axes parallel to those of the replaced durene molecule, that the principal axes of the zero-field splitting tensor are parallel to the molecular axes and that g

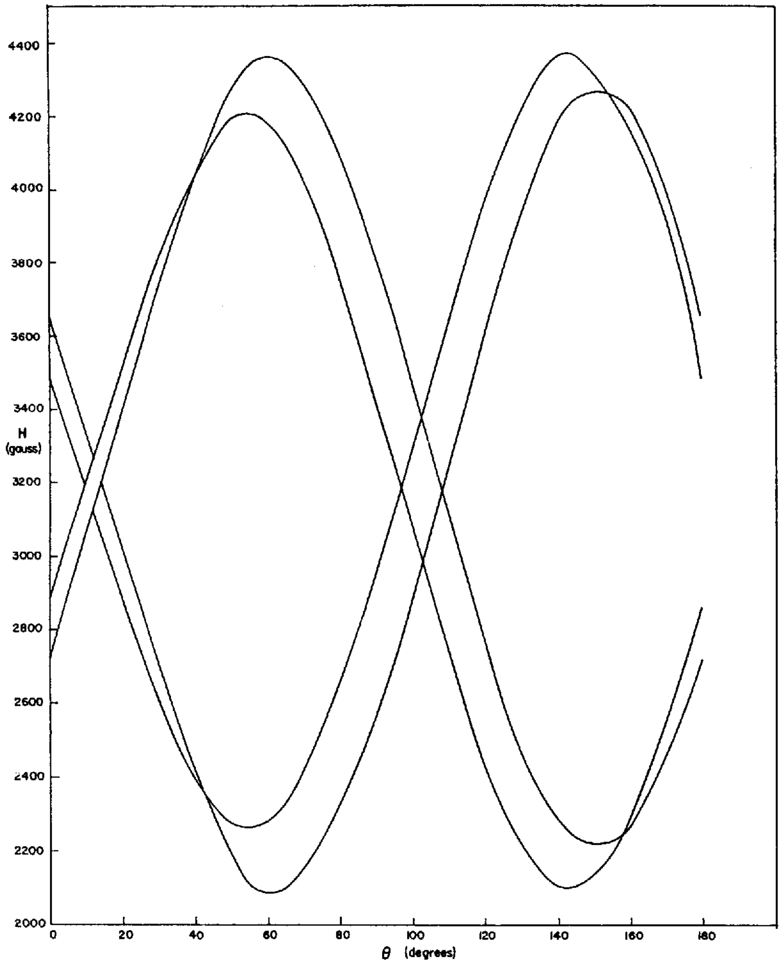

Figure 5. The variation in the magnitude of H for resonance with rotation of a mixed crystal of phenanthrene$_{h-10}$ in durene at − 180 °C about the c' crystallographic axis.

is isotropic, no consistent set of values for the zero-field splitting parameters D and E are obtained. With the values of D and E, $D/hc = \pm 0.10043$ and $E/hc = \pm 0.04658 \text{ cm}^{-1}$, determined from measurements on mixed crystals of phenanthrene in biphenyl and fluorene,[10] and adhering to the above set of assumptions, the field strengths at the stationary points have been calculated. They disagree with the observed values which are between 100 and 200 gauss less extreme. This implies that one or more of the above assumptions is at fault. The error is not in the selection of the values of D and E. These are not expected to change sufficiently from one host to another to account for the disagreement. Moreover an identical experiment for the well characterized system of naphthalene in durene was undertaken to check the experimentation. Excellent agreement with reported results was obtained. Thus, one must conclude that the phenanthrene is not substituted in the durene lattice with its molecular axes aligned parallel to those of the replaced durene molecule. As the molecular axes are rotated away from an orientation in which the L and N axes are coplanar with the *ab* crystallographic plane the stationary points, that is the maxima and minima, in the curves of Fig. 5 are expected to collapse. This is in fact what is observed since the curves have collapsed by 100 to 200 gauss relative to the theoretical case of no change in orientation. No attempts to ascertain the actual orientation of the phenanthrene in the durene crystal by rotating the magnetic field in other than the three readily obtained crystallographic planes *ab*, *bc′* and *ac′* were undertaken.

To confirm that the phenanthrene was responsible for the ESR spectra the lifetime of the triplet state was measured, 3.4 ± 0.4 sec. This agrees with other reported measurements for phenanthrene.[18,19]

Discussion

Not only will a change in the orientation of the guest molecule in the host lattice significantly modify both the theoretical oriented gas and mixed crystal polarization ratios but the accompanying lattice distortions will also have a marked effect on the mixed crystal polarization ratios. In general an ignorance of the magnitude of this modification implies an ignorance of the validity which can be assigned to observed and calculated polarization ratios. For the system phenanthrene in durene the vibrational analysis indicates a long-axis polarized transition. Furthermore, support for the assignment of the transition as long-axis polarized comes from a comparison of the theoretical and observed polarization ratios. The close agreement for the b/a polarization ratios and the observed increase in the absorption intensity parallel to c' axis are the most general effects to be expected for a small change in guest orientation. That the change in guest orientation is only small relative to the *ab* crystallographic plane can be viewed from the magnetic resonance spectra of Fig. 5 which are not widely different from the expected ones for no change in orientation.

A general result which is borne out by this study and by the investigations on multiplet structure in the spectra of mixed crystals is that where the molecular dimensions of the guest are small relative to the vacated site, multiplet structure may be expected as in chrysene in terphenyl.[20] On the other hand where the molecular dimensions of the guest are large multiplet structure is less likely but changes in guest orientation are expected as in phenanthrene in durene.

In distinction to the mixed crystal systems naphthalene and phenanthrene in biphenyl,[10] where the guests are aligned with all their molecular axes parallel to one another but not to the host, the mixed crystal systems naphthalene in durene and phenanthrene in durene do not have the guests aligned with all their axes parallel to one another. Instead the naphthalene follows the orientation of the replaced durene molecule while the phenanthrene does not.

Acknowledgements

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Appendix

(i) Durene direction cosines

	L	M	N
a	0.655	− 0.118	0.746
b	0.750	− 0.021	− 0.661
c'	0.097	0.993	0.075

(ii) Oscillator strengths

Phenanthrene	3000 Å	(L)	$f = 0.2$
Durene	2780	(L)	$f = 0.002$
	2030	(M)	$f = 0.13$
	1800	(L and M)	$f = 0.6$

(iii) Dipole–dipole interactions ($\mathrm{cm}^{-1}\,\text{Å}^{-2}$). Sum over 130 Å.

	set 1–set 1	set 1–set 2
L–L	− 209.6	1326.7
L–M	391.5	219.5
L–N	1719.9	451.7
M–M	15.3	− 904.7
M–N	387.7	309.6
N–N	197.2	1420.1

Molecule 2 is derived from molecule 1 by a screw axis rotation about *b*.