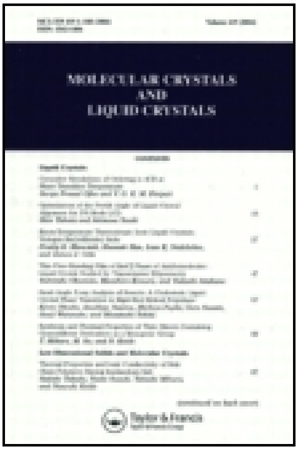

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The Dynamic Structures of Acenaphthalene and the Acenaphthalene-(S) Trinitrobenzene Complex in the Solid State[†]

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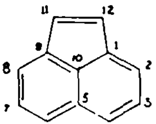
Wide-line NMR measurements indicate that the acenaphthalene molecules in solid acenaphthalene and in the molecular complex with s-trinitrobenzene show considerable mobility in the solid state. The motion, thought to be movement of the molecule in its plane about an axis of order greater than two occurs on the n.m.r. timescale at ~ 130°K in the case of acenaphthalene, and ~ 170°K in the case of the complex. The results are discussed with respect to other available physical data on the compounds, including attempted crystal structure determinations by X-Ray diffraction.

INTRODUCTION

Acenaphthalene (1) was chosen for study, as it was noted that there was no crystal structure data available in the literature for this very simple, commercially available polycyclic aromatic compound, although such structures were available for much more complicated polycyclics.



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[†] Presented at the Canadian Institute of Chemistry Annual Meeting, Halifax, (1971).

[§] From the M.Sc. thesis of G.J. Kupferschmidt, (1971), presented in partial fulfillment of the degree requirements.

Due to the inherent lack of symmetry of the molecule (in particular, lack of a centre of symmetry), any movement in its molecular plane would introduce extreme disorder, and make the crystallographic determination difficult and also deceptive (since the site might be centrosymmetric), especially if no disorder were suspected. On the premise that this might be the reason for the lack of crystal structure data, it was decided to investigate the solid using wide-line NMR and other techniques†. Such techniques have been useful in providing data complementary to that from X-ray diffraction.[1]

EXPERIMENTAL

Acenaphthalene (Aldrich Chemical Co.) was found to contain acenaphthene as an impurity. Because of their similar melting points (96° and 92° respectively), and solubility properties it was impossible to purify the sample by conventional means. The crude sample was converted to its picrate complex, and it was found that good separation of the two complexes resulted from recrystallization. The complex mixture was recrystallized six times, at which point the melting point was constant and high resolution n.m.r. showed no detectable impurities.

acenaphthalene – picrate (yellow) m.p. = 201.2°C
acenaphthene – picrate (orange) m.p. = 162°C

The complex was then decomposed with concentrated ammonia and the acenapthalene extracted with chloroform. The chloroform extract was evaporated and the resulting residue eluted through an alumina column with n-pentane. Evaporation of the pentane then yielded pure acenapthalene m.p. = 93°C.

(Note: Since it is not possible to purify this compound well by conventional means, and since the impurity is most easily detected by high resolution n.m.r., literature data prior to the introduction of this technique must be treated with some caution).

Trinitrobenzene (Eastman) was recrystallized from carbon tetrachloride to a constant melting point of 121°C (lit = 121-122°C). The acenaphthalene-trinitrobenzene complex was prepared by mixing equimolar quantities of the two components in hot chloroform. The solution was cooled and the yellow crystals of the complex filtered off, m.p. = 219-220°C, (lit. m.p. = 221°C). Chemical analysis verified that the stoichiometry of the complex was 1:1.

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† Since the completion of this study, personal communication from Dr. T. R. Welbery, has made available partial crystal structure data. This will be referred to subsequently.

EQUIPMENT

Solid-state n.m.r. spectra were recorded as first derivatives at 100 MHz using a suitably modified Varian HA-100 D spectrometer.[2] The compounds were packed into 12 mm o.d. tubes and temperatures recorded directly from a thermocouple embedded into the sample. Several spectra were recorded at each temperature and the average parameters chosen. Second moments were calculated by a numerical procedure and corrected for the effects of modulation.[3] All calculations were performed using an I.B.M. 360/50 computer. Thermodynamic measurements were made using a Perkin-Elmer differential Scanning Calorimeter Model-IB and a proper adiabatic calorimeter constructed on the premises.[4]

RESULTS AND DISCUSSION

(1) Solid State NMR Results

The proton resonance of acenaphthalene was found to be very temperature dependent (Figure 1, inset). At room temperature the signal is very narrow, suggesting the presence of some motional process. As the temperature is decreased, it gradually broadens, reaching a limiting low temperature value at 120°K. The

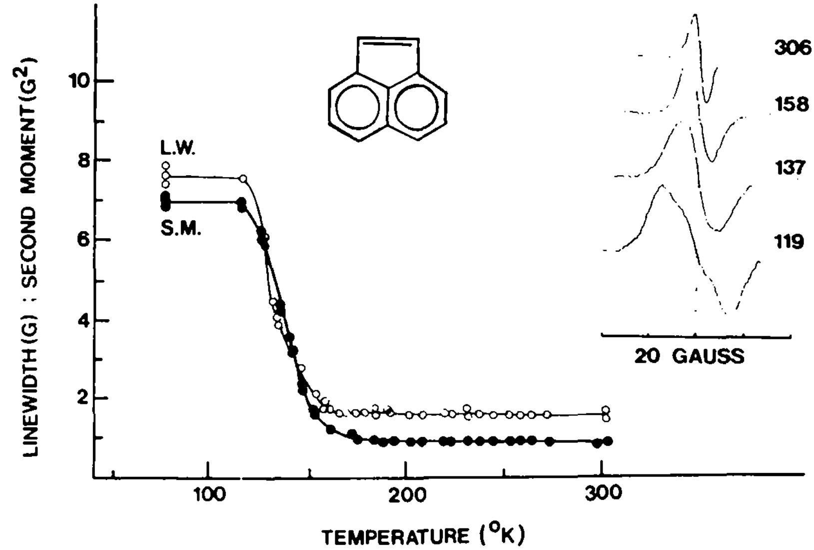

FIGURE 1 The linewidth (open circles) and second moment (filled circles) parameters of the proton resonance of acenaphthalene as functions of temperature, with (inset) representitive spectra recorded at the temperatures indicated.

experimental linewidths and second moment parameters show a clear transition centred at about 134°K, decreasing sharply from a low temperature value of 7.0 $gauss^2$ at 120°K to a high temperature value of 0.9 $gauss^2$ at 140°K, with little subsequent change up to the melting point.

The theoretical value for the rigid-lattice second moment can be calculated from the formulation of van Vleck.[5] The second moment thus calculated can be divided into two contributions; an intramolecular contribution from the nuclei on one molecule, and an intermolecular contribution from the effect of the nuclei on all the other molecules. In the absence of crystal structure data, the intramolecular second moment can be calculated with a fair degree of accuracy from the carbon skeleton of acenaphthalene, giving a value of 2.5 $gauss.^2$ This leaves ~ 5 $gauss^2$ for the intermolecular contribution to the second moment, which is in the range commonly observed for polycyclic aromatics (benzene 6.4 $gauss^2$, naphthalene 6.9 $gauss^2$, pyrene 4.25 $gauss^2$), and it is though that at low temperatures the molecules are quite rigid in the lattice†.

The most likely motion to give the large observed drop in the line-width and second moment parameters at ~ 130°C would seem to be rotation of the molecule in its plane. Rotation in this plane by 180° around a "pseudo" two-fold axis would give no reduction in the intramolecular contribution to the second moment, and the limiting high temperature value would have to be > 2.5 $gauss^2$, The observed value of 0.9 $gauss^2$ would seem to preclude such a motion. Motion about a "pseudo" axis of order > 3 would reduce the intramolecular contribution to ~ 0.8 $gauss^2$, and the intermolecular contribution could well be reduced below 1 $gauss^2$ giving a value in the approximate range of that observed. Thus it is to be expected from the N.M.R. results that acenaphthalene will exhibit a highly disordered site occupancy at room temperature. It should be noted that the averaged intramolecular second moment for a molecule undergoing reorientation is the same for free rotation about an axis as it is for a jumping motion between sites, and although the latter is considered much more probable, the unambiguous distinction between the two processes must come from some other source.

The proton resonance of the acenaphthalene-trinitrobenzene complex is also very temperature dependent (Figure 2). The large change in line-width and second moment parameters at 170°K is again attributed to motion of the acenaphthalene molecule in its plane about a "pseudo" axis of order > 3 and it is predicted

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† Calculations on the low temperature structure data communicated by Dr. R. Wellbery (6) give values of S.M. (intra) = 2.8 $gauss^2$, S.M. (inter) = 5.6 $gauss^2$ in agreement with the results quoted above. Due to the uncertain nature of the high temperature disordered structure, it is not possible to do a more exact calculation than that presented above for the case where motion is present.

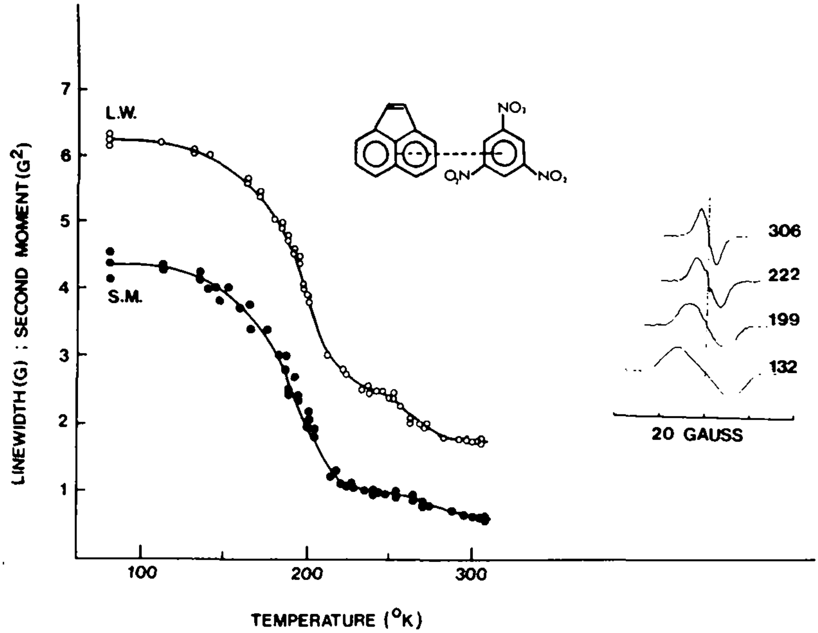

FIGURE 2 The linewidth (open circles) and second moment (filled circles) parameters of the proton resonance of the acenaphthalene-trinitrobenzene complex as functions of temperature with (inset) representitive spectra recorded at the temperature indicated.

that a very disordered room temperature structure will also be found in this case by crystallographic techniques.

Other Measurements

Spin-lattice relaxation time measurements on both acenaphthalene and the acenaphthalene-TNB complex yield very temperature dependent values of T_1. The general temperature dependence in both cases is characteristic of the presence of molecular motion, in agreement with the slow passage experiments, and the data yield approximate values of less than 10 kcal m^{-1} for the activation energies of both compounds. These measurements are currently being made with much improved temperature control in order to compare them with results from low-temperature adiabatic calorimetry (see on) and will be presented in full at a later date. The case of acenaphthalene is complex and indicates that more than one barrier to reorientation is present.

D.S.C. measurements were made from 150°K up to the melting point (366°K). No thermal anomolies were found in this range, in agreement with the

N.M.R. data where the linewidth and second moment changes occurred at ~ 134°K. (Because the nmr measurements are kinetic in nature, and the thermodynamic measurements those of a system at equilibrium, the nmr changes will occur at a temperature equal to, or higher than that of the thermodynamic anomaly.) From the d.s.c. measurements the entropy of fusion in 8.79 cal. deg^{-1} m^{-1}. This is lower than that of acenaphthalene (13.7 kcal deg^{-1} m^{-1})[7] which differs only in the presence of two extra hydrogen atoms on carbons 11 and 12, and fits well into a correlation between the occurrence of molecular motion and low enthalpies of fusion (Table I). Specific heat measurements on acenaphthalene by low temperature adiabatic calorimetry[4] indicate the presence of a strong higher order transition centred at about 124°K in agreement with the n.m.r. data. The nature of this transition, together with its relation to the relaxation time measurements, is currently under investigation.

TABLE I

Summary of motional behaviour in the solid state and measured entropies of fusion for selected polycyclics

	Motional State	Ref.	ΔS(fusion)/R	Ref.
Benzene	Moves	(11)	4.25	(15)
Pyrene	Moves	(12)	4.93	(16)
Coronene	Moves	(13)	——	—
Acenaphthalene	Moves	present work	4.42	present work
Acenaphthene	Stationary	present work	6.85	(7)
Naphthalene	Stationary	(11)	6.48	(17)
Anthracene	Stationary	(14)	7.09	(18)

CONCLUSIONS

The nature of the motional process can be deduced to some extent by comparison of the n.m.r. results with other relevant data. Thus attempted X-ray analysis[6,8,9] have yielded the space group P_{bam} (or Pba_2) at 25°. Exact structures were not determined, presumably because of disorder, but it has been suggested that the molecules lie at centrosymmetric sites,[8] giving an average site occupancy which is centrosymmetric. Assuming that the site occupancy must indeed be centrosymmetric, several possible ways of obtaining this are illustrated in Figure 3. (If the occupancy is not centrosymmetric, the situation will be more complicated still)

The simplest way of obtaining a centrosymmetric occupancy would be turning the molecule in its plane by 180° (Figure 3A). However, as discussed above, this particular type of motion is ruled out by the n.m.r. data. The next simplest way would be by rotation by 90° (Figure 3B), around a "pseudo" four-fold axis, the intermediate case of a pseudo three-fold axis being ruled out because it is not centrosymmetric. *Any* even-ordered pseudo-axis of order > 2 would also suffice. However, although motion about the centre of symmetry of the napthalene moiety is indicated in (Figure 3A) and (Figure 3B) would yield the "simplest" disordered structures because a large proportion of the atoms would be in positions previously occupied by similar atoms, a more probable axis for reorientation is probably the centre of gravity of the molecule which corresponds closely to the carbon atom at the junction of the three rings.† Motion around this axis by 180° and 90° would produce *much* more severe disorder, yielding Figure 3C, Figure 3D respectively. Of these, the n.m.r. data rules out the occupancy illustrated in Figure 3C.

However, the situation is more complicated still. The low temperature structure data of Wellbery[6] indicate that these are *three* different sites for the acenaphthalene molecules, of occupancies 2:1:1. Because of the different site symmetries, each of these types might choose a different way of obtaining the centrosymmetric site occupancy in the disordered room temperature structure, Although a "pseudo two-fold axis" such as Figure 3C is ruled out in general by the n.m.r. date, it might be possible for one of the sites with smaller numbers of molecules to even adopt this, its contribution to the spectrum being swamped by that of the remaining 75% of the molecules.

Thus it is predicted that the room temperature crystal structures of acenaphthalene and its complex with trinitrobenzene will show *extreme* disorder in the acenaphthalene molecules, being even more complicated than discussed above if it is not centrosymmetric. Of the two, the structure of the complex should be the simpler to solve, as considerable refinement could be done on the trinitrobenzene moiety which might be expected to be rigid. Such an approach has been successful in the case of the azulene trinitrobenzene complex where the azulene molecule is disordered.[10]

In the case of acenaphthalene, there will be considerable difficulty at room temperature because of the extreme disorder and also the presence of large thermal errors from the vibrations of the molecules within the disordered sites (with the relatively low activation energy for the motion, these thermal vibrations might well be large). In this case, it is thought that the best data would

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† Potential energy calculations based on the low temperature structure and using non-bonded atom-atom potential functions (4) suggest strongly that the centre of gravity is the point around which the molecule rotates.

be obtained at a temperature just above the transition, say ~ 140°K, where the disorder would be present, but when the thermal errors would be at a minimum. The use of low temperature techniques in X-ray crystallography will yield better data in many cases, even where disorder is not present.

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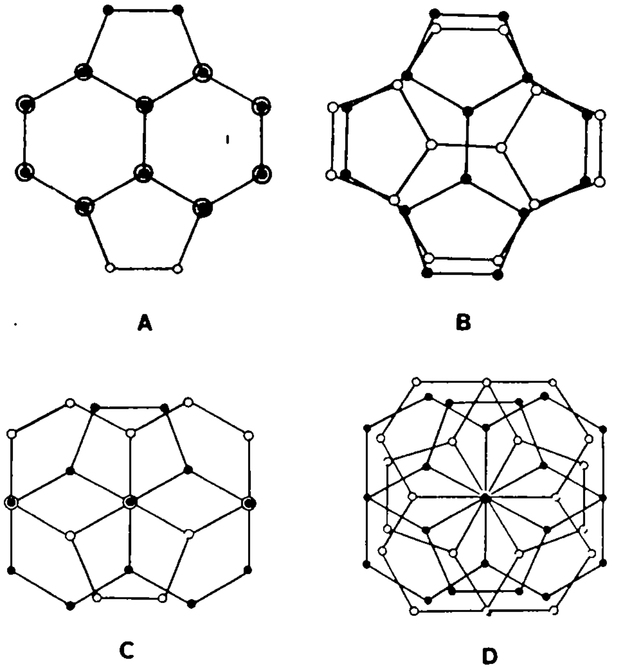

FIGURE 3. Schematic representation of the statistical site occupancy caused by the movement of an acenaphthalene molecule in its plane

(A) Around an axis through the centre of the C_{10}·C_5 bond by 180°.
(B) Around an axis through the centre of the C_{10}-C_5 bond by 90° jumps.
(C) Around an axis through the centre of gravity of the molecule (which corresponds approximately to C_{10}) by 180°.
(D) Around an axis through the centre of gravity of the molecule by 90° jumps.

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