in the remaining octahedral voids yields rock-salt, the orthorhombic sub-group of which is MO, *Immm*, $a \sim 4{\cdot}1$, $b \sim 2{\cdot}85$, $c \sim 5{\cdot}7$ Å, $Z = 4$. Another sub-family has general composition $M_{2n}O_{n-1}[T_nO_{3n+1}]$, yielding for $n = 1$, 2, 3, respectively, spinel, Mg_2SiO_4– II and manganostibite.

Systematic topological analysis of such families of atomic arrangements, both real and hypothetical, should afford closer insight into the crystal chemistry of high pressure phases for which the dense packing of equal spherical anions plays a major part. Combination of such topological analysis with geophysical data should prove valuable in elucidating the crystal structures of minerals from the Earth's mantle. Perhaps very subtle differences resulting from the interaction of outer orbital electrons determine preference between the various possible models.

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[1] Ringwood, A. E., and Major, A., *Earth Planet. Sci. Lett.*, 1, 241 (1966).
[2] Akimoto, S., and Sato, Y., *Tech. Rep. Inst. Solid State Physics*, The University of Tokyo, Ser. A, No. 328 (1968).
[3] Ringwood, A. E., and Major, A., *Earth Planet. Sci. Lett.*, 1, 351 (1966).

Lowering of the Melting Point of Molecular Layers observed by Nuclear Magnetic Resonance

SOME years ago we showed[1] that the melting points of molecular layers spread over solid surfaces are lower than the melting points of the bulk substances. The melting point may be lower by as much as 30° C and depends on the nature of the substance, the number of molecular layers spread over the solid surface and the nature of the solid support. Monolayers show maximum lowering, while after a coverage of four to ten layers the melting points reach their bulk values. This phenomenon is a general property of all substances.

We determined the melting points of the molecular layers by finding the temperature at which layers lost their ability to cause crystallization of a supercooled melt of the same substance. At this temperature the layers can no longer be considered to be in a solid state. The monolayer is the critical coverage at which the nucleation

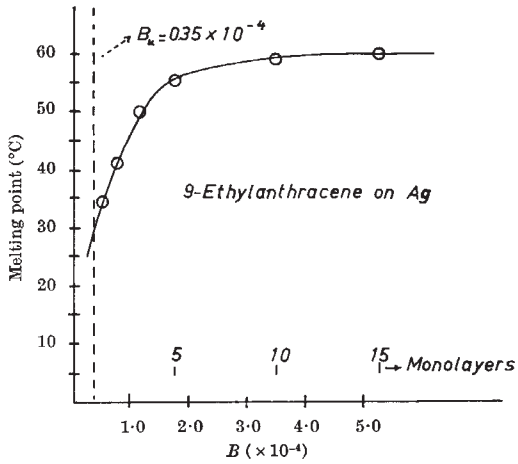

Fig. 1. The melting points of molecular layers of 9-ethylanthracene spread over Ag powder.

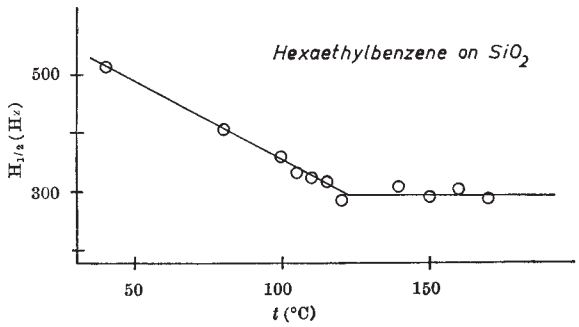

Fig. 2. The line width of a monolayer of hexaethylbenzene on SiO_2 as a function of temperature. The intercepting point at 113° C lies 16° C lower than the melting point of the bulk hexaethylbenzene.

activity first appears. At lower coverages the samples are inactive at all temperatures. Fig. 1 shows, as a typical example, the lowering of the melting point of molecular layers of 9-ethylanthracene spread over the surface of finely divided silver powder. B is the coverage expressed in grams substance per gram solid and B_K the critical coverage.

Among the regularities observed and described earlier[1] was the correlation of melting point lowering with density of π-electrons. In the case of silver–tin alloys the amount by which melting point is reduced is governed chiefly by the availability of non-occupied energy states of electron gas in the metal. This indicates that the impinging of the π-electrons into the empty energy states is responsible for the loosening of the binding between the molecules in the crystal lattice spread over the metal surface.

We have now tried to follow these phenomena by using nuclear magnetic resonance (NMR). It is known that the line width is connected to the mobility of the molecules by the relation[3]

$$\Delta\nu \approx \frac{\eta}{T}$$

where η is the viscosity of the medium and T the temperature. It would be expected on measuring the line widths as a function of the temperature that at the melting point, where an increase of the mobility of the molecules occurs, a corresponding sudden change of the line width would be observed. We have prepared samples of monolayers of hexaethylbenzene and α-naphthylamine spread over the surface of SiO_2 ('Syloid', specific surface 651 m^2/g), using the technique described previously[2]. The NMR spectra consisted of very broad peaks containing the transitions of the CH_2 and CH_3 protons of hexaethylbenzene and the transitions of the amino and ring protons of α-naphthylamine, allowing no distinction of fine structure. The narrowing of the peaks on raising the temperature ranges from 500 to 270 Hz for hexaethylbenzene and from 450 to 250 Hz for α-naphthylamine. The intensity of the peaks observed with the *A*–60*A* Varian instrument at these low coverages is very weak, so the use of a time averaging computer, model Varian *C*-1024, was necessary. By averaging the spectra over 20 and 30 sweeps, very well pronounced maxima could be observed.

Figs. 2 and 3 show the line widths at half maximum as a function of the temperature. The curves consist of two straight lines of different slopes intercepting at distinct temperatures. The mean accuracy of the line width points is ± 20 Hz[4]. The curves intercept 16° lower than the bulk melting points for hexaethylbenzene and 11° for α-naphthylamine. We consider these intercepting points to be the melting points of the monolayers. In the case of α-naphthylamine a comparison of these results with the lowering observed by the nucleation method is possible. The latter method shows a lowering of 9° while the former

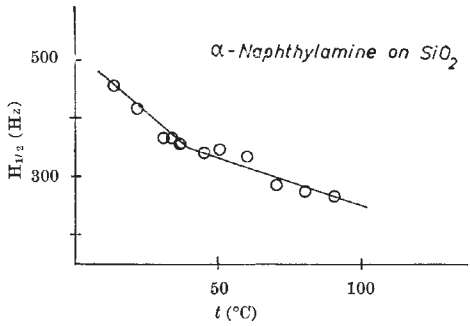

Fig. 3. The line width of a monolayer of α-naphthylamine on SiO_2 as a function of temperature. The intercepting point at 39° C lies 11° C lower than the melting point of the bulk α-naphthylamine.

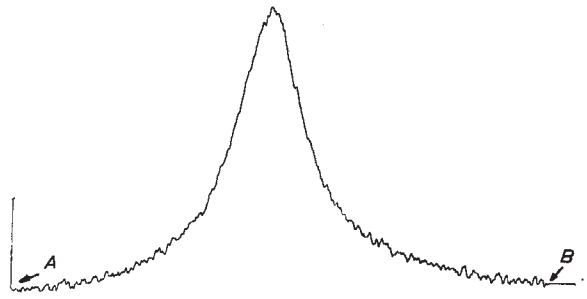

Fig. 4. Time averaged NMR spectrum of hexaethylbenzene on SiO_2 at 120° C. Number of sweeps = 10. $A-B$ = 2,000 Hz.

shows a lowering of 11°, the difference lying within the error limits of the two methods. For hexaethylbenzene the comparison of the melting points by the two methods was not possible because of the difficulties of preserving a supercooled melt of hexaethylbenzene.

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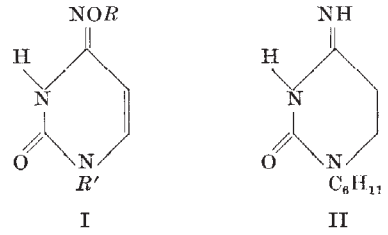
[1] Karagounis, G., *Helv. Chim. Acta*, **37**, 805 (1954). Deronane, E. G., *Ampere Colloquium* (1968).
[2] Karagounis, G., *Helv. Chim. Acta*, **36**, 282 (1953).
[3] Bloembergen, N., Purcell, E. M., and Pound, R. V., *Phys. Rev.*, **73**, 796 (1948).
[4] Karagounis, G., and Gutbrod, M., *Praktika Acad. Athens* (October, 1966).

Hydrogen-bond Association of *N*(4)-Hydroxycytosine with Purines

RECENT spectroscopic work has shown that in aqueous solution pyrimidines and purines form vertical stacks with no evidence of in-plane hydrogen-bonding between pairs of bases[1,2]. The conformations of polynucleotides in aqueous solution are probably largely determined by the interactions responsible for the vertical stacking of monomeric species[3]. In non-aqueous solution, vertical stacking is much less important[1,4], and studies of mixtures of the nucleic acid bases indicate specific hydrogen-bonding between those pairs of bases that are complementary in DNA[4–10]. In solvents which are not hydrogen-bond donors, regardless of polarity, the association constant for the guanine–cytosine pair is several times greater than that for the adenine–thymine (uracil) pair, but in both cases the mixed complex is preferred to a mixture of self-dimers; mixtures of non-complementary bases show no association, although mixed hydrogen-bonded pairs can in principle be drawn.

While complementarity is a universal feature of double stranded nucleic acids, it is by no means certain that the specific base interactions are directly involved in replication. On the assumption that they are involved[11], elaborate replication mechanisms have been proposed[12] to account for the fact that spontaneous mutations occur with a much lower frequency than can be accounted for by the presently accepted tautomeric constants. The strength of bonding involving rare tautomeric forms, however, has not been considered. For example, although the imino form of cytosine could in principle bond with adenine, the interaction may be so weak that the lifetime of the complex is very short or the bond lengths very long; incorporation of cytosine would then occur only very rarely. In any discussion of mechanisms of spontaneous or induced transition mutation it is essential that the strength of feasible interactions be considered.

The mutagen hydroxylamine[13] converts cytosine into *N*(4)-hydroxycytosine residues (I; R=H), *inter alia*, and it has been suggested that this may account, at least in part, for its GC→AT type mutagenic activity, particularly in T4 phage[14]. We have studied the interaction of *N*(4)-hydroxy-1-cyclohexylcytosine (I; R=H, $R'=C_6H_{11}$) with 5′-acetyl-2′,3′-isopropylideneadenosine by infrared spectroscopy, following the method of Kyogoku *et al.*[7,8]. Spectra of mixtures of the two compounds in carbon tetrachloride at 20° C using various molar ratios (total concentration 0·0001 M) were not additive. The absorption around 3,480 cm^{-1} was greater than could be accounted for by adenine self-association and was maximal for a 1 : 1 solution. The interaction was weak, however, and the insolubility of the *N*(4)-hydroxy compound prevented study in more concentrated solution. Because the *N*(4)-hydroxy group should play no part in the association and in addition it is known that methoxyamine is mutagenic, a similar study was made with the more soluble *N*(4)-methoxy-1-methylcytosine (I; $R=R'=$Me)[15] and the adenine derivative (total concentration 0·001 M). This again clearly showed a 1 : 1 association. In contrast, spectra of mixtures of *N*(4)-methoxy-1-methylcytosine and 9-ethylguanine showed no difference from additivity at a concentration of 0·005 M in a mixture of carbon tetrachloride and deuteriochloroform.



I II

Analysis of the data by the method of Kyogoku *et al.*[7,8] led to values of 120 l. $mole^{-1}$ for the association constant of *N*(4)-methoxy-1-methylcytosine and the adenine derivative, and 40 l. $mole^{-1}$ for the adenine self-interaction. The latter figure is lower than the value (83 l. $mole^{-1}$) obtained by Küchler and Derkosch[9] for the adenine–adenine association in carbon tetrachloride, but the evidence shows the preference for pairing of the *N*(4)-methoxycytosine with adenine over self-association, and the lack of association with guanine.

These results correlate with the fact that *N*(4)-hydroxy-(and methoxy-) cytosine derivatives exist predominantly in the oximino tautomeric form (I) (K_T about 10)[15] and emphasize their uracil-like character. From the standpoint of base-pairing, the conversion of a cytosine to an *N*(4)-hydroxycytosine residue in DNA should be conducive to a C→T transition on replication.