carried out as follows: as soon as possible, four drops of heavy water were successively placed on the sample thermistor and the moment at which the fourth drop was placed on the thermistor was chosen as zero time. Readings started after about 90 sec and the decrease of ΔR was followed for about 2 times $T_{1/2}$. A typical plot is shown in Fig. 1. The reproducibility of $T_{1/2}$ is about ± 10 per cent with a mean value of 350 sec, as was foreseen, but the reproducibility of ΔR_0 readings is 1·0–1·5 per cent (Table 1).

The theoretical values of the vapour pressure of heavy-water mixtures P_m are deducible from the following relationship:

$$P_m = P_{\mathrm{H_2O}}\,\gamma_{\mathrm{H_2O}} + P_{\mathrm{HDO}}\,\gamma_{\mathrm{HDO}} + P_{\mathrm{D_2O}}\,\gamma_{\mathrm{D_2O}} \qquad (3)$$

where γ_i is the molar fraction of compound i and P_i its vapour pressure. The value of γ_i can be deduced from the mole percentage of deuterium (x) with respect to the total hydrogen, and the value of the equilibrium constant of the reaction: $H_2O + D_2O \rightleftarrows 2HDO$.

Therefore:

$$P_m = P_{\mathrm{H_2O}}(1 - x)^2 + 2P_{\mathrm{HDO}}x \,.\, (1 - x) + P_{\mathrm{D_2O}}x^2 \qquad (3')$$

Using the P_i values reported in ref. 3, we obtain for our case:

$$\frac{\Delta P}{P_{\mathrm{H_2O}}} = -\,0{\cdot}003\,x^2 + 0{\cdot}115\,x$$

where $\Delta P = P_{\mathrm{H_2O}} - P_m$

This equation is plotted in Fig. 2 together with experimental ΔR_0 values, normalized to 2·91 × 10^3 (see also Table 1). The agreement between calculated and experimental data is good, so that the method described may be considered practicable, especially in view of its rapidity and the small volume of sample required.

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Carbonium Ion Mechanism and Results of Solvolysis of (+)-2-Bromo-octane

THE remarkable prevalence of re-arrangement in simple alkyl groups during the formation of alkyl halides, and the concomitant loss in optical purity have been loosely ascribed to the intermediate formation of a carbonium cation[1]. The conversion of an alkyl halide into the alcohol, ester, or ether must therefore be scrutinized for points of correlation. There are few published examples of alkyl rearrangement in the solvolysis of straight chain alkyl halides. Isopropanol was formed in the mercury catalysed solvolysis of *n*-propyl bromide in aqueous formic acid, and the carbonium ion mechanism was postulated[2].

By a mechanism designated 100 per cent S_N1 (that is, the carbonium ion mechanism) (+)-2-bromo-octane was solvolysed in 60 per cent aqueous ethanol at 80°, resulting in the formation of (−)-2-octanol showing some 60 per cent loss in optical purity[3,4]. It remained to be seen if rearrangement of the alkyl group also occurs in this system. We find by gas-liquid chromatography[5] that isomerically pure 2-octanol and ethyl 2-octyl ether were obtained when 2-bromo-octane (M/40) was heated under reflux (72 h) in 60 per cent aqueous ethanol. In another example, with (+)-2-bromo-octane, α_D^{20} + 40·24° ($l = 1$) (0·31 molar instead of M/40) the (−)-2-octanol, b.p. 77·5°/10 mm, n_D^{20} 1·4256, α_D^{18} − 3·62° ($l = 1$) showed 51 per cent loss in optical purity, but was accompanied by only < 0·5 per cent rearranged products. It is true that hydrogen bromide is a product of the solvolysis; but (+)-2-octanol lost no optical purity when it was heated under reflux (72 h) with 60 per cent aqueous ethanol containing hydrobromic acid (0·155 molar).

We have therefore an example of a system involving considerable loss in optical purity, previously attributed entirely to the carbonium ion mechanism, yet showing no rearrangement in the alkyl group.

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Photodimerization in Crystalline 9-Cyanoanthracene

ROBERTSON[1] has pointed out that the type of crystal structure adopted by an aromatic molecule appears to depend on the molecular shape. Thus, those in the form of elliptical planes crystallize with an anthracene-type (*A*) structure on which weak coupling between molecules in the electronically excited state is responsible for a slight shift in the fluorescence spectrum with respect to the molecular spectrum, and the vibrational structure is largely preserved. Disk-shaped molecules such as pyrene and coronene, on the other hand, exhibit strong coupling with a close-packed type *B* structure in which pairs of molecules present as a structural 'unit' or as an imperfection are responsible for the emission of the characteristic excimer band, red-shifted by some 6,000 cm^{-1} from the molecular spectrum and devoid of vibrational structure[2].

It has been shown[3] that a change in the molecular shape of anthracene by the substitution of a 9-cyano group or phenyl groups in the 9,10 positions produces a change from the molecular to the excimer fluorescence spectrum which is undoubtedly due to a corresponding change in the crystal structure from type *A* to type *B* (ref. 4). In the former case the replacement of the green structureless-fluorescence by a blue structured 'molecular' fluorescence spectrum during exposure to ultra-violet radiation was attributed[3] to the photochemical consumption of dimeric exciton traps, the logical alternative photomorphic change being difficult to visualize.

We have now taken X-ray diffraction photographs of powdered 9-cyanoanthracene in its original green-fluorescent form and of the blue-fluorescent photoproduct together with that of the photodimer precipitated from a saturated outgassed solution in toluene during exposure to ultra-violet radiation. From a comparison of the Guinier photographs shown it is clear that crystalline 9-cyanoanthracene undergoes photodimerization which may be promoted by strong interaction in the lowest excited singlet state of the close-packed type *B* structure. The blue, structured fluorescence of the photoproduct must originate from residual molecules of 9-cyanoanthracene dispersed in the photodimer matrix.

Although the photodimerization of anthracene itself in solution is well known[5], there is no reported evidence for this process in its (type *A*) crystal form. It therefore appears that in so far as molecular shape determines the type of lattice adopted by an aromatic molecule, this may also influence its photochemical behaviour in the crystalline state. It must also be concluded that, since photodimerization competes with excimer fluorescence, these two processes cannot be associated with parallel and