

To investigate structural effects, basicities are comparable only when all are obtained using the same solvent. The values of K_b' obtained in water show that increasing alkylation tends to result in increased basicity in alcohols. For example, K_b' increases methanol < ethanol < isopropanol < *tert.*-butanol and from ethanediol to butane-2,3-diol. Presumably this is due to the inductive electron-release effect increasing the electron availability, and hence the proton affinity, of the hydroxyl oxygen. Conversely, the electron availability and proton affinity of the oxygen atom would be expected to be reduced by the presence of an electron attracting group in the molecule: such a group is the hydroxyl group, and K_b' decreases from ethanol to ethanediol. Again the electron availability would be expected to be greater at an ethereal oxygen than at an alcoholic oxygen, and accordingly dioxan has a high basicity. Ethyl acetate exhibits a basicity greater than acetone and dioxan: here, the acyl group will tend to reduce the proton affinity of the alkoxy oxygen, and the high basicity may be due to the protonation occurring on the carbonyl oxygen in the ester.

The values of K_b' in Table 1 vary overall by a factor of ten. This suggests that structural effects, such as discussed here, are only of secondary importance and that solvation effects on the ionic and non-ionic species predominate.

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Presence of Polarization Bonds in some Copper(II) Complexes

CRYSTAL structure determinations have shown that although the co-ordination of the metal in molecules of *bis*acetylacetonatocopper(II)¹, *NN'*-ethylenebis(acetylacetonimine)copper(II)² and *bis*salicylaldehydatocopper(II)³ is essentially square planar the molecules pack such that there is an axial approach (that is, perpendicular to the co-ordination square) of 3.1–3.4 Å from the copper to a

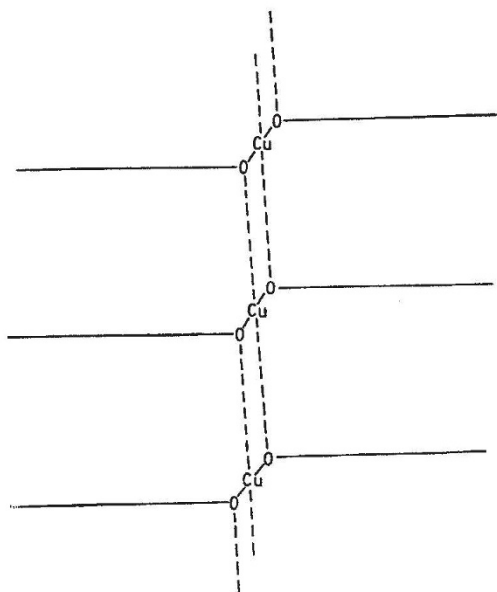


Fig. 1

conjugated region of an adjacent molecule. Whereas such an intermolecular approach is not abnormally short it is accompanied by a distinct distortion of the molecules from their expected shape, clearly indicating that there is an interaction between them. It has been suggested that these are examples of polarization bonding, the π -bond system acting as an electron donor and the copper atom as acceptor⁴.

We have determined the crystal structures of *bis*(*N*-methyl-2-hydroxy-1-naphthaldiminato)copper(II) (*A*) and a second crystal modification of *bis*salicylaldehydatocopper(II) (*B*). Both exhibit the same type of intermolecular approach to the hydroxy oxygens of neighbouring molecules (2.94 Å and 3.15 Å, respectively) and the same type of deviation from overall molecular planarity. Within one molecule the two ligands are individually planar but mean planes through them are separated by 1.16 Å and 0.36 Å (Fig. 1). A similar molecular distortion was observed in the previously reported modification of *bis*salicylaldehydatocopper(II) (*C*). The distortions indicate that definite, though weak, interactions exist and we suggest that again polarization bonds occur in these compounds.

Crystal data for the compounds *A*, *B* and *C* are given in Table 1. In the structures of both *A* and *B* the positions of the copper atoms were determined by space-group requirements, and the lighter atoms were located from heavy atom phased three-dimensional Fourier syntheses. Refinement has proceeded by successive difference Fourier syntheses to present *R*-factors for observed planes of 0.159 and 0.164, respectively.

	<i>a</i>	<i>b</i>	<i>c</i>	β	Space group	<i>Z</i>	Colour
<i>A</i>	3.86	19.55	12.57	91.1°	$P2_1/n$	2	brown
<i>B</i>	11.75	4.00	12.42	90.3°	$P2_1/c$	2	green
<i>C</i>	8.72	6.20	11.26	104.8°	$P2_1/n$	2	green

It is of interest to note that the polarization bonds can involve different regions of the salicylaldehydato ligand, being to an oxygen of the chelated ring in *B* and to a carbon of the benzene ring in *C*, and it would appear to be this factor which stabilizes the two different forms. We are at present studying a further brown modification of *A*.

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Dehydration of Calcium Silicate Hydrate (C-S-H(I))

THE reported formation of beta dicalcium silicate (β -Ca₂SiO₄; Ca/Si = 2.0, abbreviated to β -C₂S) during the dehydration of C-S-H(I) (Ca/Si 0.5–1.5) (in carbon dioxide-free air controlled at a water vapour partial pressure of 6 mm of mercury)¹ seemed to indicate that the crystal structure of C-S-H(I), which has not been completely described, might be related to the known crystal structure of β -C₂S.

A survey of the literature reveals that all the large number of compounds in the system CaO—SiO₂—H₂O become dehydrated (to give anhydrous calcium silicates) in the temperature range 300°–800° C, under approximately the same conditions as the foregoing, and that