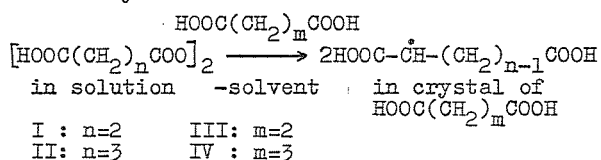


04.4-2 FREE RADICALS LONG-LIVING IN CRYSTAL MATRICES OF DICARBOXYLIC ACIDS. X-RAY STUDY OF PEROXYDISUCCINIC AND PEROXYDIGLUTARIC ACIDS. By S.V.Lindeman, V.E.Shklover, Yu.T.Struchkov, E.K.Starostin, G.I.Nikishin, Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, Moscow, USSR.

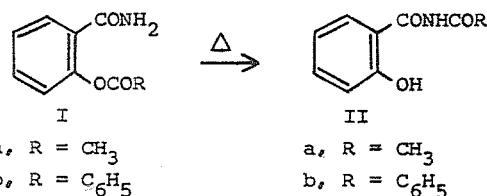
Cocrystallization of peroxydisuccinic acid (I) with succinic acid (III) and peroxydiglutaric acid (II) with glutaric acid (IV) results in the formation of crystal phases with a high concentration of free radicals which according to ESR data is equal to 6.10^{19} and 2.10^{17} spin/g respectively. At ambient conditions the life time of these radicals is not less than one year.



In order to elucidate the mechanism of formation and stabilization of these radicals and, in particular, to clarify the observed difference of their concentrations in the matrices of III and IV we carried out an X-ray study of I and II (the structures of III and IV were determined previously by J.M.Robertson). The crystal structures of I and III are very similar. The corresponding unit cell axes differ approximately by integer numbers with a similar character and orientation of hydrogen-bonded chains of molecules. This quasi-isomorphism of I and III possibly favours an incorporation of molecules I into the crystal structure III with substitution of two molecules III by one molecule I in hydrogen-bonded chains. However, lattice strains, inevitably arising on such substitution, should lead to destabilization of molecules I with a break-up into free radicals which are trapped in the crystal matrix of III. The structures of II and IV are also similar, but the difference of their unit cell axes are greater than in the case of the I-III pair. Possibly this is the reason of the smaller concentration of free radicals formed on cocrystallization of II with IV.

04.4-3 SOLID STATE ACYL MIGRATION IN SALICYLAMIDES. AN X-RAY STUDY OF THE O- AND N- BENZOYL DERIVATIVES. By K. Vyas and H. Manohar, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India.

Studies on thermally induced acyl migration in the solid state from O- to N- position in the salicylamides are of current interest.



The structures of Ia and IIa and a possible mechanism on the basis of crystal packing were reported (V. Mohan Rao and H. Manohar, XII International Congress of Crystallography, Ottawa, 1981). The studies have now been extended to a series of acyl derivatives. We report the structures of Ib and IIb, in which system the reaction takes place around 120°C in solid state.

The crystal data are : Ib, $\text{C}_{14}\text{H}_{11}\text{NO}_3$, Monoclinic, $\text{P}2_1/\text{c}$, $Z = 16$, $a = 18.974(2)$, $b = 25.902(4)$, $c = 10.126(3)\text{Å}$, $\beta = 93.87(2)^\circ$. Presently R is 0.123 for 3668 reflections. IIb, $\text{C}_{14}\text{H}_{11}\text{NO}_3$, Monoclinic, $\text{P}2_1/\text{n}$, $Z = 4$, $a = 4.886(5)$, $b = 18.474(4)$, $c = 13.099(7)\text{Å}$, $\beta = 98.29(5)^\circ$. Presently R is 0.148 for 1104 reflections.

The asymmetric unit of the reactant, Ib, contains 4 independent molecules with different conformations and they are packed as pairs of hydrogen-bonded dimers. The bond formation between the amide nitrogen and acyl carbon atoms is the principal step in the reaction. The N...C distances within the molecules are in the range of 3.3 to 3.9Å, satisfying the distance criterion for the reaction to occur (M.D. Cohen and G.M.J. Schmidt, J. Chem. Soc., 1996 (1964) and the following papers). On the other hand, the intermolecular N...C contacts are all greater than 5.0Å. Thus, as in the acetyl derivatives an intramolecular mechanism appears likely. The molecule IIb is essentially planar as is Ib. Details will be presented.