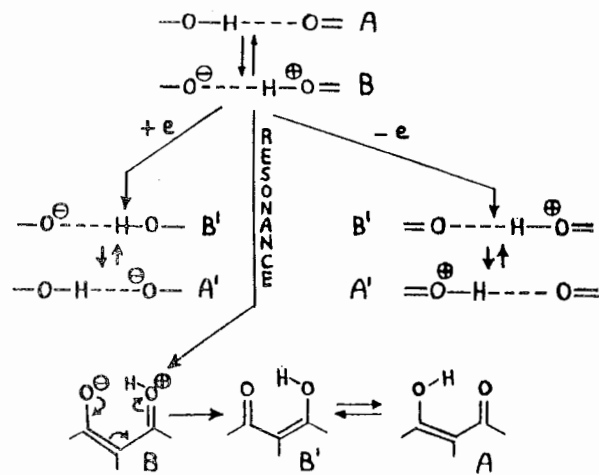


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connecting the two O atoms by a resonant system able to transmit the charges; (ii) by adding an electron to B; (iii) by removing an electron from B (see scheme). Experimental proves of such statement will be given at the meeting for all strong O-H...O bonds retrievable from the Cambridge Structural Database.

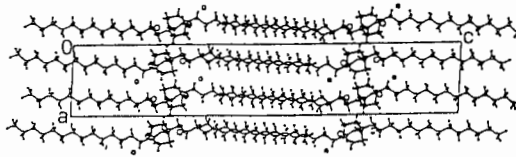


PS-06.04.08 QUATERNARY ALKYL HALIDE SALTS OF 1,4-DIAZABICYCLO[2.2.2]OCTANES WITH HALIDE ANION CONDUCTIVITY. By M. Yasui¹, R. Yamazaki¹, F. Iwasaki¹, T. Nogami¹, N. Kamiya² and H. Iwasaki², ¹Dept. of Applied Physics and Chemistry, The Univ. of Electro-Communications, Chofu, Tokyo 182, Japan, ²The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan.

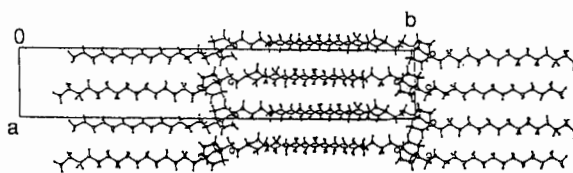
A series of quaternary alkyl halide salts of 1,4-diazabicyclo[2.2.2]octanes (DABCO) exhibited first-order phase transition in the temperature range of 62-100°C and showed halide anion conductivity in the high temperature phase (Shimizu, J. *et al.*, 1986, Bull. Chem. Soc. Jpn, **59**, 1443-1448). The phase transition temperature (T_c) and heats of transition showed a so-called even-odd number effect of carbon number which was also observed for a series of long chain alkanes and alcohols. In this study, we have investigated the crystal structures of *N,N'*-ditetradecyl-1,4-diazabicyclo[2.2.2]octane dibromide (I) and a dipentadecyl derivative (II). In each crystal, one dimension of the unit cell was very long and crystals showed instabilities against the X-ray irradiation, so that the intensity data from single crystals were collected on the IPD-WAS (Weissenberg type diffractometer with Imaging Plate, N. Kamiya *et al.*, 1990, Acta Cryst. **A46** Suppl., C10). The molecular structures of (I) and (II) have similar features. Two alkyl chains have *trans*-zigzag conformation, and dihedral angles between the planes of alkyl carbons are 128 and 157° for (I) and (II), respectively. Two bromide anions reside near the DABCO ring. Alkyl chains form sheet-like structures in crystals. In spite of the difference of chain length, the number of van der Waals contacts between alkyl chains in (I) is slightly larger than that in (II). This fact may explain the even-odd number effect that the heat of transition of (I) was greater than that of (II). In the powder X-ray diffraction patterns for (I) and (II) which were measured at the temperature near T_c, sharp diffraction peaks for the high temperature phase appeared at lower 2θ angles. At the temperature beyond the T_c, diffraction peaks assigned for short axes directions disappeared, although the sharp peaks for long axis direction still remained. Thus disorder along short axes just as the liquid-crystal arose from the phase transition.

Crystal Data

| | (I) | (II) |
|----------------------|--|---|
| Formula | 2Br ⁺ C ₃₄ H ₇₀ N ₂ ²⁻ · 0.5H ₂ O | 2Br ⁺ C ₃₆ H ₇₄ N ₂ ²⁻ |
| Fw | 666.75 | 694.80 |
| Color | Colorless | Colorless |
| Crystal system | monoclinic | orthorhombic |
| Space group | P2 ₁ /c | P2 ₁ 2 ₁ 2 ₁ |
| a/Å | 8.720(1) | 8.792(5) |
| b | 8.789(2) | 52.046(7) |
| c | 49.298(8) | 8.727(2) |
| β/° | 93.83(2) | 90.00 |
| V/Å ³ | 3770(1) | 3993(1) |
| Z | 4 | 4 |
| Reflections measured | 9499 | 10125 |
| observed | 3675 | 2385 |
| R | 0.0650 | 0.0650 |



(I)



(II)

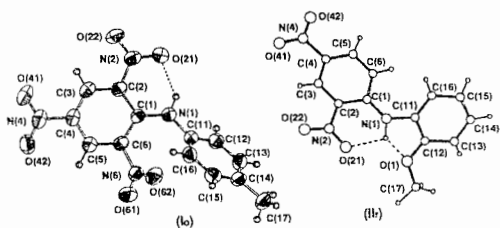
PS-06.04.09 POLYMORPHIC STRUCTURES AND PHASE TRANSITIONS OF N-PICRYLANILINE DERIVATIVES. By K. Taguchi, M. Hirota, K. Maeda, M. Yasui and F. Iwasaki*, Dept. of Applied Physics and Chemistry, The Univ. of Electro-Communications, Chofu-shi, Tokyo 182, Japan

N-picryl-*p*-toluidine (I) and *N*-(2,4-dinitrophenyl)-*o*-anisidine (II) crystallize in two modifications, orange and red forms. The condition to crystallize each form is very subtle, so that it is by chance which form can be obtained and the coexistence of these forms is often observed. The orange crystals of both I and II turns red just below the melting points. After the orange crystals melt completely, the red crystals are obtained by cooling. Crystal structures of these polymorphic forms have been determined in order to study on the relationships between molecular interactions and polymorphic transition.

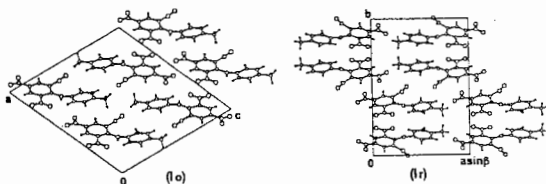
| | I _o | I _r | II _o | II _r |
|------------------------------------|--------------------|--------------------------|--------------------|-----------------|
| Color | Orange | Red | Orange | Red |
| Cr. system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Sp. group | P2 ₁ /a | P2 ₁ /c | P2 ₁ /a | P2 ₁ |
| a / Å | 16.475(3) | 13.107(4) | 15.546(8) | 15.693(2) |
| b | 6.007(1) | 17.739(4) | 4.220(1) | 10.981(3) |
| c | 15.203(3) | 6.090(2) | 16.747(4) | 3.842(1) |
| β / ° | 114.12(1) | 102.16(3) | 122.31(1) | 98.39(2) |
| V / Å ³ | 1373.2(4) | 1384.2(8) | 1287.0(7) | 655.0(2) |
| Z | 4 | 4 | 4 | 2 |
| D _x / gcm ⁻³ | 1.539 | 1.527 | 1.493 | 1.467 |
| Radiation | MoKα | MoKα | CuKα | MoKα |
| No. ref. | 2188 | 1434 | 1234 | 866 |
| R | 0.052 | 0.106 | 0.120 | 0.079 |
| Solvent | acetone | acetone+CCl ₄ | benzene+EtOH | acetone |

The molecular structures of I_o and I_r are very similar. Intramolecular NH...O hydrogen bond is formed between anilino and nitro groups. On the other hand the molecules of II_o and II_r are rotational isomers. In II_r NH group is hydrogen-bonded to nitro and methoxy groups bifurcatedly, while in II_o the hydrogen

bond between NH and OMe groups can not be formed because the *o*-methoxyphenyl group is rotated by 180°.



In order to study on the dynamic behavior of the conversion from the orange to red forms powder diffraction was measured for **I**. Powder diffraction pattern of the red crystals obtained from the melting sample of **Io** is the same as that of **Ir** recrystallized from solution. Temperature dependence of the diffraction patterns showed the drastic conversion from the orange form to the red form just below the melting point. The orange form undergoes a thermal rearrangement into the red.



PS-06.04.10 THE INFLUENCE OF THE SYMMETRY OF MOLECULES ON THEIR ARRANGEMENT IN CRYSTAL. By *K.A.Potekhin** & *P.M.Zorky*, Chemical Department, Moscow State University, Moscow, 119899, Russia.

Though the native symmetry of a molecule (i.e. symmetry of an isolated molecule) is usually lost in the space group of a crystal except the inversion center, it is, as a rule, partially or completely retained in the pseudosymmetry groups of some molecular agglomerates (chains, layers, spatial substructures) or even of the whole structure. Thus, this symmetry influences substantially the packing of molecules. This influence was studied for a few crystal structures and the variety of the pseudosymmetrical molecular examined. The formation of the latter can be successfully interpreted using the method of potential functions symmetry (MPFS). Sometimes it is useful to divide the crystal into so-called molecular cells for revealing the pseudosymmetrical sub-systems. As a very interesting example two polymorphs of 2,3,7,8-tetramethyl-1,4,6,9-tetraselenaspiro[5,5]nona-2,7-diene investigated by X-ray method recently (Potekhin K.A. et al., to be published) are discussed. The polymorph which exists at room temperature is pseudotetragonal but its exact symmetry is $C2/c$. At -84°C it transforms into a triclinic form. This transformation consists of a small shift of molecules and the crystal structure retains the pseudotetragonal and pseudomonoclinic symmetry.

PS-06.04.11

THE TWINNED CRYSTAL STRUCTURE OF TETRAIODOADAMANTANE, $\text{C}_{10}\text{H}_{12}\text{I}_4$ by Gautam R. Desiraju, D. Sekhar Reddy, School of Chemistry, University of Hyderabad, Hyderabad 500 134, India, A. David Rae* and Donald C. Craig, School of Chemistry, University of New South Wales, PO Box 1, Kensington N.S.W. 2033, Australia

The structure crystallised in spacegroup $I4_1/a$, $a=b=7.1984(7)$, $c=28.582(4)$ Å, $Z=4$, 295 K, with individual molecules of implicit $\bar{4}2m$ symmetry on sites of $\bar{4}$ symmetry in the crystal and was refined using a twin/disorder model to $R=0.030$ which may be compared to a previous untwinned model of Bremer, Gregory & von Rague Schleyer, *J. Org. Chem.* (1989) 54 3796-3799 which refined to $R=0.20$. The structure may also be compared to the *Olympic rings* structure of adamantane-1,3,5,7-tetracarboxylic acid, Ermer, *J.A.C.S.* (1988) 110 3747-3754.

The shortest I...I contact of 4.063(1) Å is between centrosymmetrically related molecules at $0, 1/4, 1/8$ and $1, 3/4, -1/8$, a vector of $a + 1/2b - 1/4c$. The $\bar{4}$ site symmetry creates a related vector $-1/2a + b + 1/4c$, the sum of the two being $1/2a' = 1/2a + 3/2b$. The cell $a' = a + 3b$, $b' = -3a + b$, $c' = c$ can be used to describe a network of molecules connected by the 4.063 Å contacts. The distribution of molecules in this network is a distorted diamond structure with 8 molecules per F centred cell. This cell has a volume 10 times that of the $Z=4$ structure in a, b, c . This gives 5 interpenetrating structures, the *Olympic Rings*.

Tetraiodoadamantane is different however in that the c/a ratio is 3.971 as against 2.915 for Ermer's structure and an idealised value of $\sqrt{10} = 3.162$. Also the molecules are rotated so that a further I...I contact of 4.167(1) Å is made between Iodines with the same z coordinate so that now all the Olympic rings touch. Each of the four Iodines of a reference molecule contacts a different network.

The twin/disorder mechanism gives useful information about the intermolecular contacts. The structure can be described in terms of 4_1 screw related layers of molecules, the symmetry of any such layer being very nearly $P\bar{4}2m$. The structure can therefore be thought of as a modulation of an idealised parent structure in which this symmetry holds exactly. In such a structure there is no reason why molecules in an adjacent layer perpendicular to c should select between origins $1/2(a+b)$ apart. If complete disorder existed a parent structure of spacegroup $C4_2/acm$ would result corresponding to $h+k$ even (l even) data, i.e. $P4_2/nmc$ for the cell $1/2(a-b), 1/2(a+b), 1/2c$. Selecting from the symmetry elements of this parent structure an Iodine at $0.3045, 0.5366, 0.05044$ could be in contact with an Iodine of a molecule in an adjacent layer by either the operation $1/2-x, 3/2-y, -z$ or $3/4-y, 5/4-x, -z$ rather than $1-x, 1-y, -z$. Both locate the adjacent molecule in the same position but the first operation creates a simple stacking fault while the second is a 2 fold rotation and corresponds to the twin rule. There was very little evidence for disorder. A disordering corresponding to the twin rule refined to the fraction 0.010(3). Distances of 4.285 Å and 4.172 Å respectively are compared to 4.063 Å. The C-I...I angles are 138.4° for the 4.063 Å contact and 144.5° for the 4.167 Å contact rather than 180° for an idealised Olympic rings structure. The angle is 134.7° for the twin related distance of 4.172 Å.