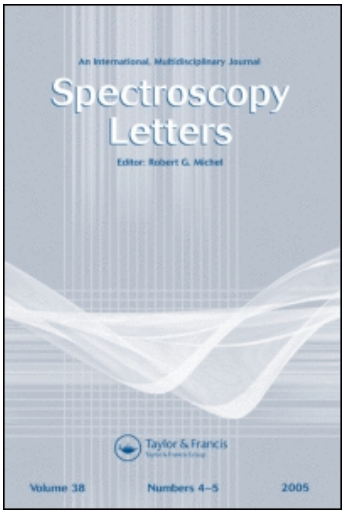

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ABSTRACT

Despite of the similar centers of chelation in phthal- and salycil-aldehydes, they react differently with hexachloro-cyclotriphosphazatriene. ^{31}P-nmr reveals evidence of symmetric substitution around the central cyclotriphosphazatriene ring explicit in a sharp resonance. ^{1}H-nmr shows a broad signal at 7.30 and at 6.80 ppm for the phenyl ring protons of the phthal and salicyl derivatives, respectively. The salicyl derivative shows, in addition, a lower field multiplet in the range 6.95–7.65 ppm. This derivative shows a longer (335 nm) wave-length π-π* transition of more mesomeric salicyl rings, compared to the more dominant π-π* transition of other

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salicyl rings of retarded mesomerism at 261 nm and to the dominant π-π* transition of the phthal derivative at 254 nm. Albeit few, these spectral findings demonstrate symmetric substitution with single type phthal rings, compared to two types of salicyl rings. Phthalaldehyde chelates using its both aldehydic protons to form the *tris*-phthal derivative, with the phthal rings being located in a plane perpendicular to the central phosphazatriene. Salicylaldehyde reacts solely via its aldehydic rather than phenolic proton in three geminal pairs; half of which locate coplanar and the other half perpendicular to the phosphazatriene. The more mesomeric coplanar salicyl ring set enhances the phosphazatriene weak π-π* transition at 204 (parent) and 210 (Phthal) nm into a higher coefficient transition at 216 nm. Consistent with this proposal of two different salicyl ring sets, the phenolic proton appears in rather two sharp ^{1}H-nmr resonances of identical integration at 10.30 and 10.75 ppm. Appearance of the latter resonances in the salicyl derivative is evidence that precludes involvement of the phenolic proton in the reaction with the central phosphazatriene ring. Ft-ir spectroscopy emphasizes the molecular complexity of these derivatives in more details; most important is the strongly absorbing $\upsilon P{<}Cl_2$ modes of hexachlorocyclotriphosphazatriene vanish upon the reaction, which verifies symmetric substitution at the phosphazatriene ring.

Key Words: Molecular structure and spectroscopy; Symmetric cyclotriphosphazatrienes

INTRODUCTION

Spectrally based structural analysis is a subject of fascinating art dedicated to Science. Spectral analysis helped in assignment of anomalous thermodynamic data for new complex compounds to their molecular structure.[1–4] It served in the establishment of the reaction mechanism for Mobil *M*ethanol *T*o *G*asoline MTG conversion over Mobil HZSM-5 catalyst.[5–7] It helped in comprehending origin of the ambiguous disturbance in the product distribution during the catalysis over boron impregnated, compared to boron incorporated in HZSM-5.[8,9] The impregnation or incorporation of boron was to modify HZSM-5 zeolite shape selectivity. This disturbance was found peculiar to catalyses involving

water that seems to mobilize the impregnated phase of boron throughout the catalysis of, for instance, toluene alkylation. Water drives boron out of the zeolite rendering the modified catalyst eventually as original. Unlike the mobile phase of impregnated boron, the incorporated phase of boron is stationary[9] that should resist the water-assisted mobility confirmed recently for the zeolite protons.[10] Variable temperature Ft-ir spectroscopy afforded key structural information of importance that helped in comprehending long debated low activity of protons, albeit are highly acidic.[11] This tool has also assisted in assigning the high ir spectral background observed for one of the fluorescing ICT complexes[12] and the fast ion conduction features observed for a material out of the fast ion conductor family[13] that turned to a dipole-protonic mediated conduction upon extending conjugation at the expense of the ion mobility in that fast ion conductor.[14] More recently, it has played a significant role in unveiling the nature of the modifier that turned acidic HZSM-5 catalyst to oxidative-acidic mediated catalyst capable of catalyzing the difficult task of methane conversion to gasoline in a multistage single catalytic process.[15]

The previous efforts correlating the spectral and structural features[1–15] have continued in the present work to shed light on diverse molecular structures of cyclotriphosphazatrienes that have been achieved upon substitution with similar aldehydes of rather different drives. Based on Freidel-Crafts synthesis, the title derivatives were prepared using proton mobility in aldehydes and mesomerism-assisted chlorine activity in hexachlorocyclotriphosphazatriene. The aldehydes were chosen to bond diversely with only minor shift in molecular symmetry. Phthaldehyde chelates via the aldehydic protons, whereas salicyladehyde bonds via the aldehydic rather than phenolic proton that would be of structural interest worth studying by such simple techniques of collaborating molecular (^{1}H & ^{31}P)-nmr, uv and Ft-ir spectroscopy.

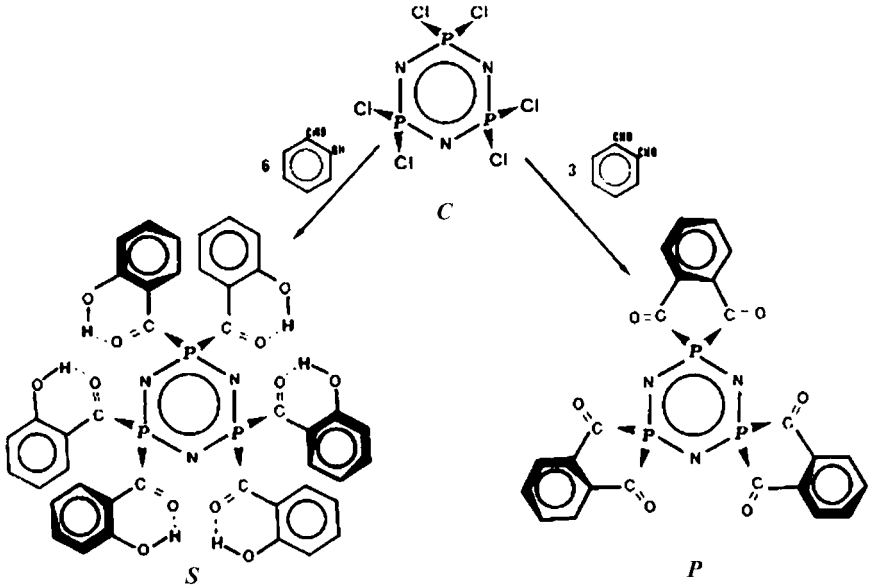
EXPERIMENTAL

Materials

The reactants were *h*exa*c*hloro*c*yclo*t*riphos*p*hazatriene, HCCTP (Nippon Soda Co. Ltd.) and phthalaldehyde or salicylaldehyde (BDH). Dry toluene was used as a reaction medium. Anhydrous $AlCl_3$ (Fluka) was applied as Freidel-Crafts catalyst. Triethylamine (Riedel de Haen) was used for removing the liberating HCl that would symmetrically protonate the basic cyclotriphosphazatriene CTP ring and could then perturb the phase purity with the relevant HCl-salt.[16]

Materials and Methods

Friedel-Crafts was applied to react HCCTP with phthalaldehyde or salicylaldehyde in dry toluene containing $AlCl_3$ catalyst for forming (Sch. I) the title phenone derivatives. Because of the reaction complexity and lower proton mobility, the salicyl (m. p. of 388 K) derivative formed in much lower rate and yield than for the phthal (m. p. of 453 K) derivative. The elemental analysis was made for N, C and H to identify the CTP and surrounding rings. The phthal derivative showed N: 7.74, C: 55.44% and H: 2.31%. Considering the molecular weight of 531 g, this makes $C_{24}H_{12}N_3$ with ca. 2% deviation from the theoretical percentages. The N_3 atoms are for the CTP ring; the $C_{24}H_{12}$ formula is for the *tris*-phthal (Sch. I_P) rings. The salicyl derivative showed N: 4.79, C: 59.57% and H: 3.56%. Considering the molecular weight of 861 g, this makes $C_{42}H_{30}N_3$ with ca. 2% deviation from the theoretical percentages. The N_3 atoms are of the CTP ring. The $C_{42}H_{30}$ formula is for the *hexa*-salicyl (Sch. I_S) rings. They were characterized by (^1H & ^{31}P)-nmr, uv and variable temperature Ft-ir spectroscopy. (^1H & ^{31}P)-nmr spectra were measured in highly concentrated solutions of DMSO-d_6 at 400 and 160 MHz for the ^1H- and ^{31}P-resonances, respectively, using a



Scheme I. Proposed molecular structures for the reaction products of HCCTP (C) with phthalaldehyde (P) and salicylaldehyde (S).

Bruker spectrometer. Uv spectra were recorded in 10^{-5} M ethanol solutions, using a Beckman Du-70 spectrometer. Ft-ir spectra were measured in the solid state, using a KBr disc matrix, a Graseby Specac variable (293–523 K) temperature cell and a Nicolet FT-IR 510P spectrometer.

RESULTS AND DISCUSSION

NMR Spectral Analysis

^{1}H-nmr spectrum of phthalaldehyde shows two resonances of singlet and multiplet structures at 10.60 and 7.90 ppm for the aldehydic and phenyl ring protons, respectively. The aldehydic signal at 10.60 ppm disappears (Fig. 1_P) upon the reaction with HCCTP, while the multiplet signal at 7.90 ppm diffuses in rather broad signal at a higher field of 7.30 ppm. Such shifts demonstrate symmetric chelation with more electronically shielded phthal rings. Healing the magnetically different phthal ring protons might explain an even exposure to the stronger field of the central CTP ring that could be allowed with a perpendicular orientation. The sharp ^{31}P-nmr resonance at -4.00 ppm verifies the symmetric (Sch. I_P) substitution.

Salicylaldehyde shows ^{1}H-nmr singlets at 11.00 and 9.80 ppm for the aldehydic and phenolic protons, respectively. The more acidic aldehyde proton is more H-bond associated. The salicyl ring protons resonate in mutiplet resonances in rather high 7.40–7.00 ppm field. The aldehydic 11.00 ppm signal disappears upon the reaction of salicylaldehyde with HCCTP. Careful investigation of the spectrum (Fig. 1_S) unveils coexistence of two overlapping patterns. In the aromatic proton field, two signals of identical integration appear in broad (6.80 ppm) and mutiplet (6.95–7.65 ppm) structures. The former signal is similar to that of the phthal derivative and therefore assigns salicyl rings of similar perpendicular orientation to the CTP. The latter signal assigns more deshielded salicyl rings of rather coplanar orientation to CTP. Salicylaldehye would then surround CTP in two sets; one set is of a perpendicular orientation similar to the phthal derivative, while the second set is of a coplanar (Sch. I_S) orientation. Consistent with this proposal of differently oriented salicyl ring sets, the phenolic proton appears in two sharp singlets of also identical integration (Fig. 1_S) at 10.30 and 10.70 ppm This would preclude participation of salicylaldehyde phenolic proton in the reaction with CTP. Such diverse orientation of the salicyl rings should not argue against symmetric substitution at the CTP ring, which is evident in the sharp signal shown solely in the ^{31}P-nmr spectrum.

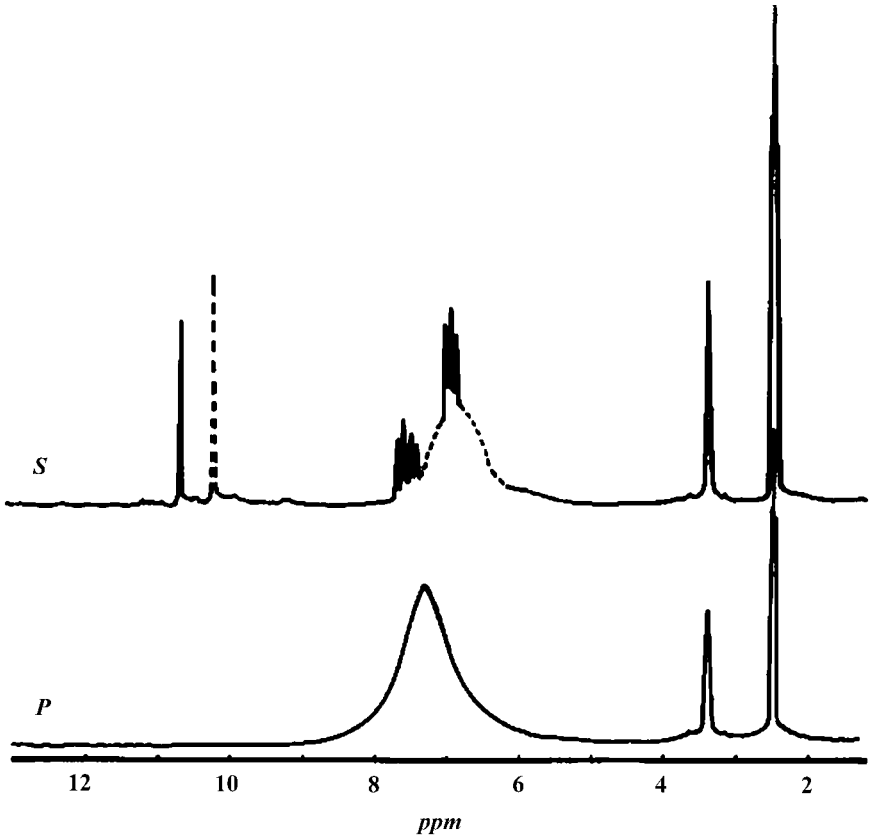


Figure 1. ^{1}H-NMR spectra (0–14 ppm) of phthal (P) and salicyl (S) CTP derivatives in DMSO-$d_{6;}$ the salicyl (S) spectrum shows overlapping profiles distinguished by solid and dashed lines. The 2.5 ppm (DMSO) and 3.4 ppm (water) resonances are of slightly hydrated DMSO. The former DMSO resonance has been used for calibrating the chemical shifts.

UV Spectral Analysis

Uv spectrum of HCCTP (Fig. 2_C) is dominated by a low coefficient band at 204 nm indicative of the low dipole CTP ring π-π^* transition.[17,18] Reaction with phthalaldehyde infers a small bathochromic shift (Fig. 2_P) of 6 nm. The phthal rings absorb in a higher dipole π-π^* transition at 254 nm. Such low wavelength transitions would be attributed to a molecular structure of retarded mesomerism (Sch. I_P) due to lacking origin of the ring coplanarity.

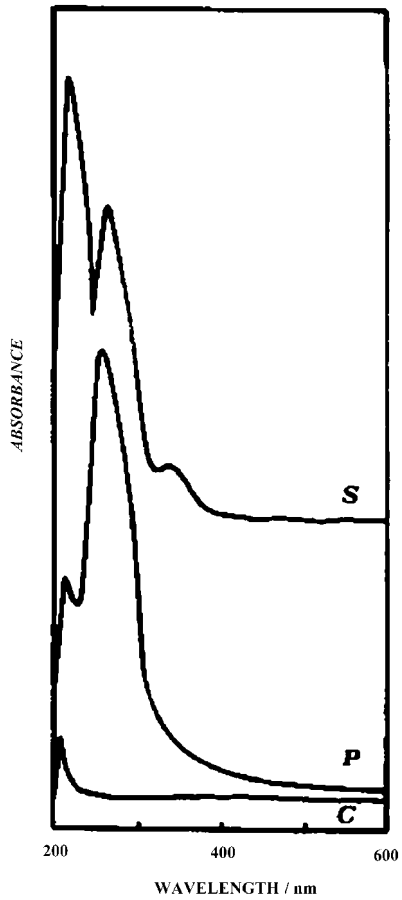


Figure 2. UV spectra (200–600 nm) of the parent chloro (C), phthal (P), and salicyl (S) derivatives recorded in 10^{-5} M solutions of pure ethanol.

At variance, greater interaction seems to have taken place with salicylaldehyde so that the CTP ring π-π* transition intensifies considerably (Fig. 2_S) at a longer wavelength of 216 nm. The salicyl π-π* transition absorbs at 261 and 335 nm; the former transition is similar to that of the phthal derivative at 254 nm and so associates with the set of perpendicular location. The longer wavelength transition must then associate with the set of the coplanar orientation. Interaction with the coplanar oriented salicyl ring set explains the notable rise in the CTP ring π-π* transition coefficient and wavelength of the salicyl derivative.

FT-IR Spectral Analysis

In the high energy 4000–2000 cm^{-1} region, the spectrum of HCCTP (Fig. 3_C) shows a non-fundamental band at 2095 cm^{-1} assigned to combination of the CTP $\upsilon_{ring\ breathing}$ mode at 1222 cm^{-1} and the less dominant ring mode 873 cm^{-1}. The combination band disappears as a result of fading the 873 cm^{-1} band that would indicate improved symmetry of the products. Substitution with bulky molecules minimizes the puckering induced in the ring of HCCTP.[19] A similar observation has recently been observed upon full substitution with phenyl rings.[16] The phthal derivative shows (Fig. 3_P) a group of $\upsilon_{C\text{-}H}$ bands in the range of 3060–2920 cm^{-1}. The salicyl derivative shows (Fig. 3_S), in addition, $\upsilon_{C\text{-}H}$band at a lower energy of 2850 cm^{-1}. The latter band complies with the more mesomeric salicyl rings located coplanar to CTP ring. The higher frequency bands associate with $\upsilon_{C\text{-}H}$ of the perpendicularly located phenyl rings commonly found in the phthal and salicyl derivative.

In the more descriptive 2000–200 cm^{-1} region, HCCTP shows (Fig. 3_C) the dominant CTP $\upsilon_{ring\ breathing}$ at 1222 cm^{-1} with non-fundamental modes at both higher and lower frequencies. Other dominant bands appear at 603 and 529 cm^{-1} for the asymmetric and symmetric $\upsilon_{P<Cl2}$. Lower intensity absorptions appear at 873 and 332 cm^{-1} for the less dominant ring modes. The phthal derivative (Fig. 3_P) shows $\upsilon_{C=O}$ at higher (1777 and 1719 cm^{-1}) energies than (1690 cm^{-1}) of phthalaldehyde. A similar shift to 1800 ± 50 cm^{-1} is observed in phthalic anhydride, the molecule of retarded mesomerism, the feature to which the present shift is also assigned. Supporting evidence to retarded mesomerism in the phthal derivative lacking ring coplanarity is explicit in upward shifts of 20 and 64 cm^{-1} in υ_{ring} of the phthal and CTP rings, respectively. A peculiar band is observed at 1464 cm^{-1} similar to the five-member skeletal band at 1460 cm^{-1} of phthalic anhydride that lends a similar assignment for the present phthal derivative. The salicyl derivative shows (Fig. 3_S) $\upsilon_{C=O}$ at typical (1660 cm^{-1}) and lower (1618 cm^{-1}) energies of salicylaldehyde. Its υ_{ring} absorbs also at similar (1590 cm^{-1}) and lower (1483 cm^{-1}) energies. The lower energy bands associate with the mesomeric salicyl set located coplanar to the CTP.

Interaction with diverse mesomerism coplanar and perpendicular salicyl sets spans a wide (1277–1157 cm^{-1}) splitting in the CTP υ_{ring} band.[20–23] The skeletal mode absorbs at 1455 cm^{-1}. The strong band observed at 758 cm^{-1}(phthal) and at 754 cm^{-1}(salicyl) is typical $\gamma_{C\text{-}H}$ mode. The salicyl derivative is distinguished by a broad $\delta_{O\text{-}H}$ band at 1340 cm^{-1} that confirms the earlier finding precluding participation of the salicyl phenolic proton in reaction with HCCTP. In accord with full substitution around the CTP ring, $\upsilon_{P<Cl2}$ vanishes in the product spectra.

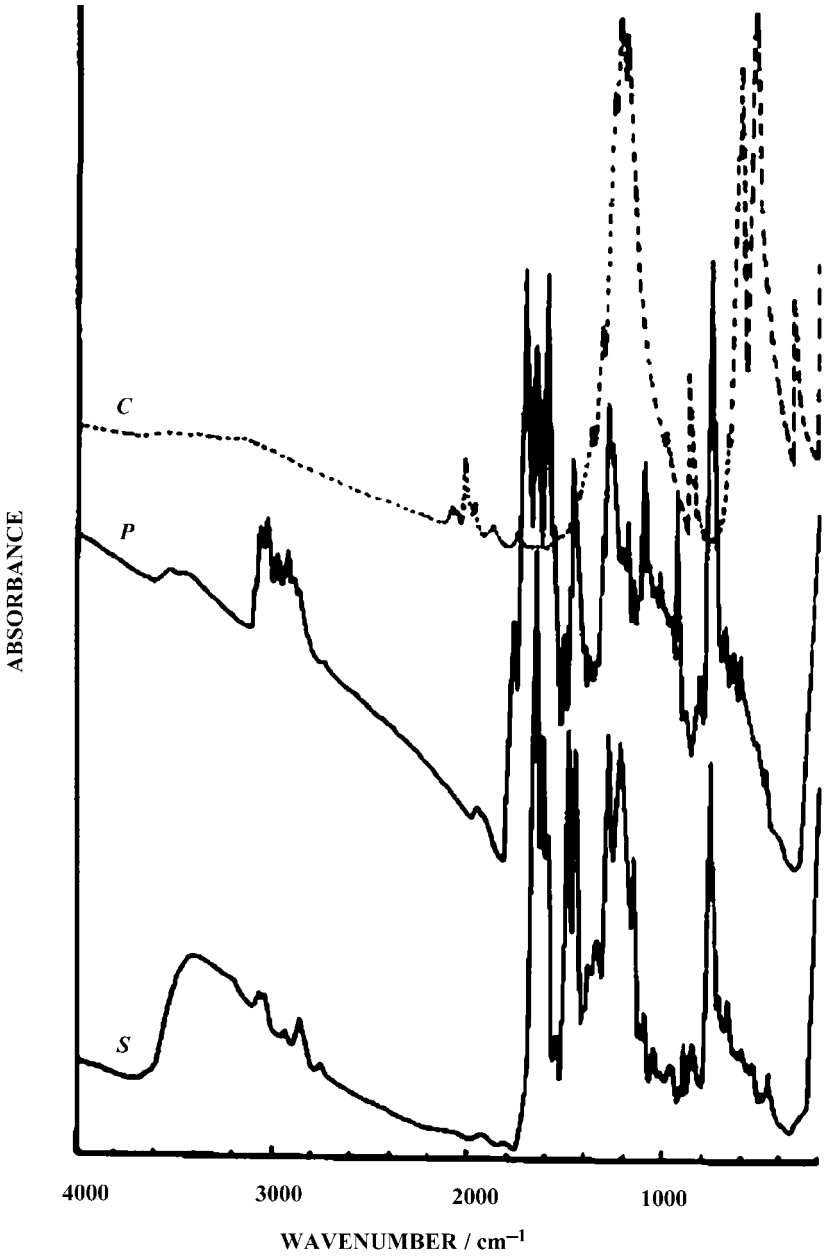


Figure 3. IR spectra (200–4000 cm^{-1}) of the parent chloro (C), phthal (P), and salicyl (S) derivatives measured in the solid state, using a KBr disc matrix.

A broad band is shown in the $\upsilon_{O\text{-}H}$ region of the phthal (Fig. 3_P) spectrum. It vanishes upon heating at 373 K and is, therefore, assigned to H-bonding contribution associating the phthal material to some of the crystallization alcoholic solvent trapped in the molecular structure.[26] At variance, the salicyl derivative shows (Fig. 3_S) a more intense band at $3390\,cm^{-1}$ shifted on heating at 423 K to $3520\,cm^{-1}$ that assigns a stronger intramolecular H-bonding association. In effect, $\delta_{O\text{-}H}$ at $1340\,cm^{-1}$ shifts to $1329\,cm^{-1}$, while $\upsilon_{C=O}$ intensifies due to loss in H-bonding. Heating raises mesomerism slightly in the salicyl derivative as explicit in a minor downward shift of $5\,cm^{-1}$ in the $\upsilon_{C=O}$ and υ_{ring}, compared to their persistence in the phthal derivative.

CONCLUSIONS

The present spectral correlation, whether performed in the solid state or in solution, has made possible structural analysis using old simple techniques of molecular spectroscopy. The small difference in proton mobility of the aldehydic and phenolic protons turns out the different tendency of chelation for the phthal- and salicyl-aldehyde. Phthalaldehyde chelates to the CTP ring, whereas salicylaldehyde does not due to the lower phenolic proton mobility. Because of chelation, phthalaldehyde enfolds the central CTP ring in a perpendicular plane. Salicylaldehyde surrounds the central CTP ring in rather more complex molecular structure. It reacts solely via the aldehydic proton leaving its phenolic proton free as spectrally evident. For stability requirements salicylaldehyde encloses the CTP ring with two sets of salicyl rings; one is of a coplanar orientation while the second is of a perpendicular location around CTP. The coplanar salicyl ring set is distinguished by lower field ^{1}H-nmr resonances, lower energy uv transition and lower energy ir absorptions, compared to the perpendicular salicyl ring set. The molecular structure of the phthal derivative is slightly perturbed by association to some of the crystallization solvent trapped in the molecular structure that can be easily removed. At variance, the salicyl derivative is highly perturbed by rather strong intramolecular H-bonding association difficult to break even at elevated temperatures.

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