

## Structure and Properties of Cocrystals of Phenazine and Fumaric-, 2,3-Dihydroxyfumaric-, and Oxalic Acid

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*Dedicated to Professor Paul Rademacher on the Occasion of his 60th Birthday*

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**Abstract.** Phenazine and the dicarboxylic acids fumaric-, 2,3-dihydroxyfumaric-, and oxalic acid form 1 : 1 cocrystals. X-ray analysis shows that the molecules are arranged as linear tapes, mainly held together by strong O-H...N and weak C(sp<sup>2</sup>)-H...O hydrogen bonds. Individual molecules form staples which are surrounded by staples of the other molecules. The angle between neighbouring tapes varies from ca. 90° in the cocrystal of phenazine and fumaric acid to ca. 70° in the co-crystal of phenazine and 2,3-dihydroxyfumaric acid, and ca. 25° in the cocrystal of phenazine and oxalic acid. The molecules assume an *offset face-to-face* arrangement in individual phenazine staples. Negligible  $\pi$ -stacking is observed

in the cocrystals of phenazine with fumaric- and 2,3-dihydroxyfumaric acid. The absence of the CC double bond as spacer in oxalic acid leads to appreciable  $\pi$ -overlap of phenazine molecules in the cocrystal. As a consequence, the latter cocrystal displays special properties. An irreversible light-induced electron transfer generates initially singlet and triplet biradicals with the unpaired electrons positioned on neighbouring phenazine molecules. Partially, the electrons are transformed to magnetically independent electrons which show strong exchange narrowing in the e.p.r. spectrum at temperatures > 0 °C. The proposed model is supported by UV/Vis-e.s.r.-, and SQUID measurements.

The design of solid state structures by cocrystallization of suitable molecules opens a route to obtain materials with special and novel properties. The spacial arrangement of the components will generally be different from that in the crystals of the individual molecules, thus leading to new solid state structures. Further, interactions between the individual components may induce new properties. The art of crystal engineering, being part of the area of supramolecular chemistry, is presently developed [1]. Our interest in this area arose from the fortuitous isolation of a cocrystal of a 1,4-bisimine and a 1,2-diol [2]. The study of this cocrystal led to the discovery of a number of similar structures of which some showed special macroscopic properties, *e.g.* a thermally reversible photochromism [3]. It was shown that the 1,4-bisimine in these cocrystals can be replaced by heterocyclic compounds providing two nitrogen atoms as hydrogen bond acceptors for the protons of hydroxy groups. Cocrystals of 1,2-diols with phenazine were isolated and it was found that the cocrystal of phenazine and *meso*-1,2-diphenyl-1,2-ethanediol exhibits a thermally reversible photochromism which is the result of a cooperative electron-proton transfer [4].

In continuation of this investigation we report on the formation of cocrystals of phenazine with fumaric acid, 2,3-dihydroxyfumaric acid, and oxalic acid, and on their

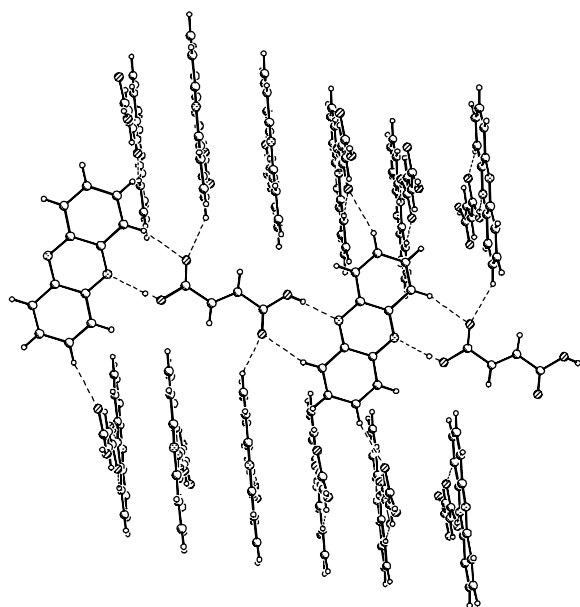
properties. Previously a cocrystal of phenazine with diacetylenecarboxylic acid had been reported in connection with a topochemical polymerization of diacetylenecarboxylic acid [5]. Further, fumaric acid was introduced in a cocrystal with a cyclic bisamidine [6] and malonic acid, 3,5-dinitrobenzoic acid, and 3,5-dinitro-4-methylbenzoic acid [7] were successfully cocrystallized with phenazine.

### Results

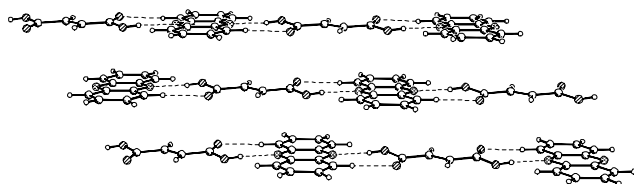
#### *Structures of Cocrystals*

**Phenazine and Fumaric Acid:** A 1:1 solution of the components in acetone yielded long, yellow needles which are 1:1 cocrystals according to the X-ray analysis solved in the space group  $P2_1/c$  with crystallographically centrosymmetric molecules of phenazine and fumaric acid. The hydroxy groups form strong O-H...N hydrogen bonds (O...N 277.2 pm, O-H...N 173°) which resembles the main linkage between both molecules resulting in chains of alternating assemblies in (1-1 -2) as can be seen in Figure 1 and 2. Distances in the observed range are quite normal for hydrogen bonds of this type [8]. Both molecules are almost coplanar (interplanar angle 7.5°) due to additional weaker C-H...O

bridges ( $\text{H}\cdots\text{O}$  238 pm,  $\text{C-H}\cdots\text{O}$   $162^\circ$ ) between the carbonyl oxygens and aromatic protons of the heterocycle. Such distances are within the region discussed as  $\text{C-H}\cdots\text{X}$  hydrogen bonds [9]. Almost perpendicular (interplanar angle  $85.9^\circ$ ) to the main motif shown in Figure 1 further chains are arranged, networked *via* further weak hydrogen bonds between the carbonyl groups and phenazine protons ( $\text{H}\cdots\text{O}$  245 pm,  $\text{C-H}\cdots\text{O}$   $151^\circ$ ). As a consequence, the chains form stacks in which the phenazine molecules are shifted which separates the centroids of the heterocyclic rings by 534.3 pm whereas the separation of the parallel chains is 317 pm. Such an offset face-to-face arrangement avoids repulsive interactions of the  $\pi$ -electrons and allows for coulombic interactions [10].



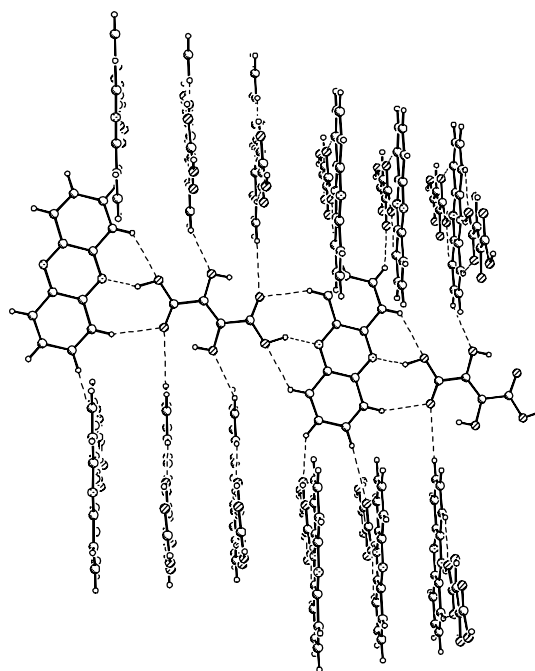
**Fig. 1** Crystal packing of phenazine and fumaric acid in the cocrystal, shown along a chain of molecules approximately along  $[1 -1 0]$ .



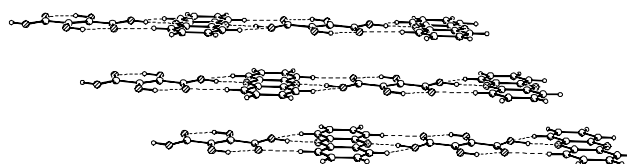
**Fig. 2** Offset face-to-face arrangement of phenazine in the cocrystal with fumaric acid, projection approximately down  $[1 1 4]$

*Phenazine and 2,3-Dihydroxyfumaric Acid:* Cocrystals were isolated as yellow needles when a 1:1 mixture was crystallized from acetone. When heated to ca.  $135^\circ\text{C}$  the cocrystals changed their colour and decomposed above  $150^\circ\text{C}$ . The crystal packing of the cocrystals in

the space group  $P2_1/c$  (Figure 3 and 4) is similar to the previous one, both crystallographically centrosymmetric molecules are almost coplanar (interplanar angle  $3.8^\circ$ ) and the  $\text{O-H}\cdots\text{N}$  hydrogen bonds ( $\text{O}\cdots\text{N}$  271.7 pm,  $\text{O-H}\cdots\text{N}$   $152^\circ$ ) which link the two molecules are slightly shorter. The carbonyl groups now form three hydrogen bridges one strong intramolecular  $\text{O}\cdots\text{H-O}$  to the hydroxy groups in the 2,3-position ( $\text{O}\cdots\text{O}$  260.6 pm,  $\text{O-H}\cdots\text{O}$   $157^\circ$ ), the one to the aromatic protons of the heterocycles ( $\text{H}\cdots\text{O}$  250 pm,  $\text{C-H}\cdots\text{O}$   $158^\circ$ ) and one which links the chains to the staples *via*  $\text{C-H}\cdots\text{O}$  bridges ( $\text{H}\cdots\text{O}$  285 pm,  $\text{C-H}\cdots\text{O}$   $177^\circ$ ). The molecules in the staples are now more tilted and form an interplanar angle of  $105.9^\circ$ . The hydroxy oxygens at the central bond of the fumaric acid are also involved in weak hydrogen bonds ( $\text{H}\cdots\text{O}$  248 pm,  $\text{C-H}\cdots\text{O}$   $144^\circ$ ) to the staples (Figure 4), in which the centroids of the phenazine molecules are separated by 530.6 pm and the distance of the chains is 317 pm.

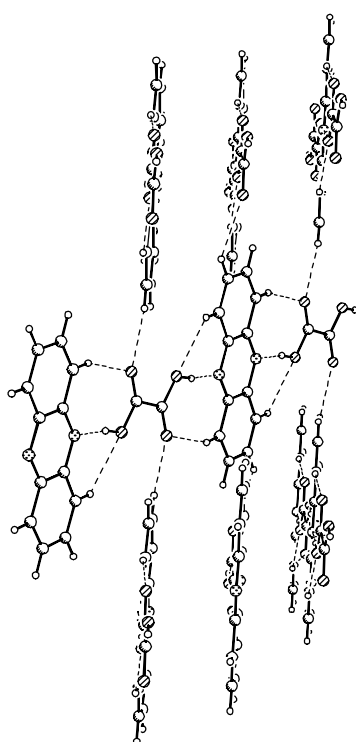


**Fig. 3** Crystal packing of phenazine and 2,3-dihydroxyfumaric acid in the cocrystal, shown along a chain of molecules approximately down  $[1 1 0]$ .

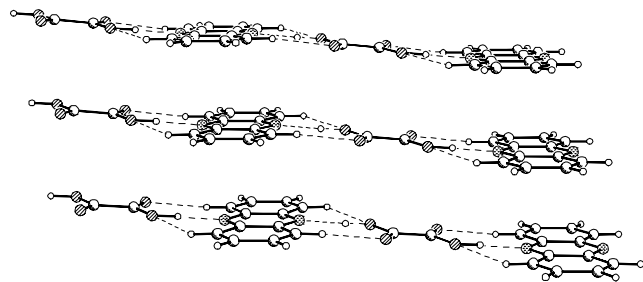


**Fig. 4** Offset face-to-face arrangement of phenazine in the cocrystal with 2,3-dihydroxyfumaric acid, projection down  $[1 0 1]$ .

**Phenazine and Oxalic Acid:** Yellow needles (*m.p.* 223 °C) were obtained when a 1:1 mixture of phenazine and oxalic acid was crystallized from acetone. The *m.p.* of oxalic acid is 189.5 °C and 182 °C for the  $\alpha$ - and  $\beta$ -form, respectively [11], while phenazine melts at 174 °C. The crystal packing of the cocrystal in the space group  $P2_1/n$  is shown in Figure 5 and is similar to the previous two. Both crystallographically centrosymmetric molecules are almost coplanar (interplanar angle 7.9°) and the O-H...N hydrogen bonds (O...N 271.9 pm, O-H...N 176°) are even stronger than the corresponding previous two. The carbonyl groups form two hydrogen bridges, one to the aromatic protons of the hete-



**Fig. 5** Crystal packing of phenazine and oxalic acid in the cocrystal, shown along a chain of molecules.



**Fig. 6** Offset face-to-face arrangement of phenazine in the cocrystal with oxalic acid, projection approximately down [1 0 1].

rocycles (H...O 244 pm, C-H...O 159°) and one which links the chains to the staples *via* C-H...O bridges (H...O 252 pm, C-H...O 129°). The molecules in the staples are now even more tilted and almost coplanar to the chains, the interplanar angle is only 26.6°. The hydroxy oxygens of the oxalic acid are also involved in weak hydrogen bonds (H...O 283 pm, C-H...O 155°) to the staples (Figure 5), in which the centroids of the phenazine molecules are now separated by only 385.5 pm and the distance of the chains is 341 pm, which corresponds to a  $\pi$ -stacking of the aromatic moieties and the sum of the van der Waals radii [12].

### Properties of the Cocrystals

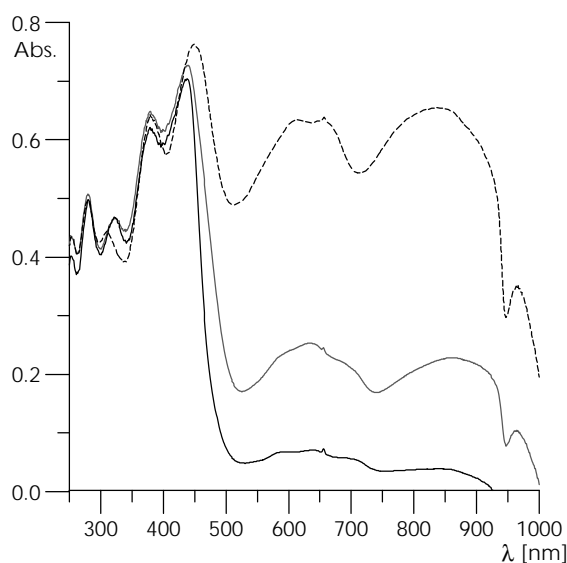
The cocrystal of fumaric acid and phenazine does not show properties which are different from those of the crystals of the individual components. The replacement of fumaric by dihydroxyfumaric acid leads to a material which undergoes an irreversible change on heating above 150 °C with destruction of the crystals, in particular in the presence of oxygen where the colour changes from yellow to green before the cocrystal decomposes. This process is accompanied by decarboxylation of dihydroxyfumaric acid as evidenced by the IR spectrum and the  $^1\text{H}$ - and  $^{13}\text{C}$  NMR spectra. In the NMR spectra of dissolved crystals only the signals of phenazine are left, dihydroxyfumaric acid is no longer present. If treated in the absence of air under argon the cocrystal changes its colour from yellow to green without decomposing on heating to >100 °C. A  $^1\text{H}$ - and  $^{13}\text{C}$  NMR analysis after dissolving the cocrystal indicates the presence of both components in the original 1:1 ratio even if held at higher temperatures for longer periods of time. Elemental analysis of such a sample also gives no indication of decomposition. The colour change is not reversible, neither by heat nor by light. At room temperature the cocrystal displays a weak paramagnetism which increases strongly when heated to 100 °C. The e.s.r. spectrum indicates two signals, a smaller ( $\approx 2$  mT wide) and a broader one (6 mT wide). When the paramagnetism of a sample heated for 90 min at 110 °C under argon is quantitated by a SQUID measurement a radical concentration of ca. 3% is obtained. The origin of this phenomenon must be due to the presence of the two hydroxy groups at the double bond, giving dihydroxyfumaric acid an endiol structure. Such compounds are called reductones, a term which indicates the easy oxidation [13]. In fact, 2,3-dihydroxyfumaric acid is an antioxidant in solution [13]. It can be assumed that the hydroxy groups render the double bond susceptible to electron transfer and that, therefore, an electron is transferred to phenazine producing a radical anion and a radical cation. Whether the radical anion is stabilized by

proton transfer from the carboxy group to the nitrogen of phenazine as in the case of the cocrystal of phenazine and *meso*-1,2-diphenyl-ethanediol [14] can not be decided due to inconclusive evidence from the IR spectrum. It seems, however, to be a possibility.

The IR spectrum of the cocrystal of oxalic acid and phenazine was compared with that of crystalline oxalic acid. The latter is characterized by a broad band for OH vibrations with intense absorptions at 3506 and 3426  $\text{cm}^{-1}$ , and a C=O stretching vibration at 1684  $\text{cm}^{-1}$ . In the cocrystal the OH vibration is shifted to wave numbers below 3100  $\text{cm}^{-1}$ , with individual bands between 2915 and 2450  $\text{cm}^{-1}$ . The carbonyl vibration is shifted 42  $\text{cm}^{-1}$  from 1684 to 1726  $\text{cm}^{-1}$ . The differences are indicative of changes in the hydrogen bonding pattern of pure oxalic acid and the cocrystal. This is also indicated by the change in the C=O double bond length in pure oxalic acid and in the cocrystal. The latter is characterized by a bond length of 118.9 pm, whereas the former shows two different bond lengths of 120.7 and 122.2 pm due to the crystal packing [14]. When the cocrystal is irradiated for 60 s with a 1kW Hg/Xe lamp (Schott GG395 and UG5 filters), a dramatic change occurs at wavenumbers  $> 2800 \text{ cm}^{-1}$ , where the transmission of the probe decreases from ca. 75% to ca. 50% without showing fine structure. The intensity of the C=O double-bond vibration decreases and new absorption bands of low intensity appear at 1277, 1301, and 1611  $\text{cm}^{-1}$ . The latter absorptions are typical for 5,10-dihydrophenazine and the 5,10-dihydrophenazyl-radical cation [15] and were also observed in the cocrystal of phenazine and *meso*-1,2-diphenyl-1,2-ethanediol [4]. Although no NH vibration can be identified in the expected region of the IR spectrum due to the strong and unstructured absorption above 2800  $\text{cm}^{-1}$  the presence of the bands at 1277 and 1301  $\text{cm}^{-1}$  can be taken as evidence for proton transfer from the carboxy group to a phenazine nitrogen atom.

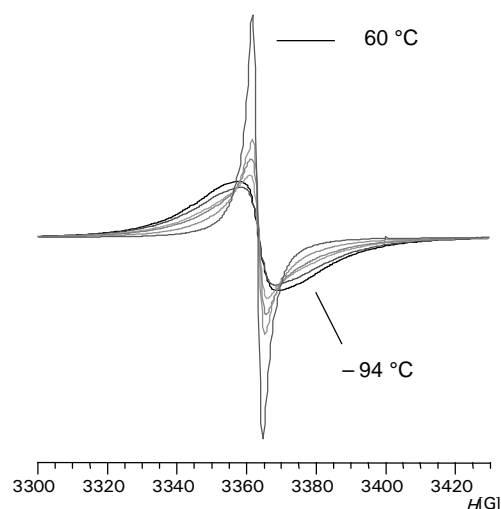
Irreversible changes in the UV/Vis spectrum on irradiation are shown in Figure 7. The longest wavelength absorption band of the unperturbed cocrystal is at 436 nm. When irradiated for 60 s two broad absorptions develop, one between 500 and 700 nm with maxima at 611 and 660 nm and another between 740 and 1000 nm with a maximum at 860 nm. The notch at 950 nm is an artefact of the spectrometer. The sensitivity of the crystal towards light exposure is so high that the new absorptions are already present when a UV/Vis spectrum of the not-irradiated sample is recorded.

On irradiation the cocrystal becomes paramagnetic. Figure 8 presents spectra which were recorded at different temperatures after irradiation at  $-94 \text{ }^\circ\text{C}$ . The rather broad band at  $-94 \text{ }^\circ\text{C}$  sharpens with rising temperature, such that at  $+60 \text{ }^\circ\text{C}$  the line width is only 0.1 mT. This is obviously due to exchange narrowing. Further infor-



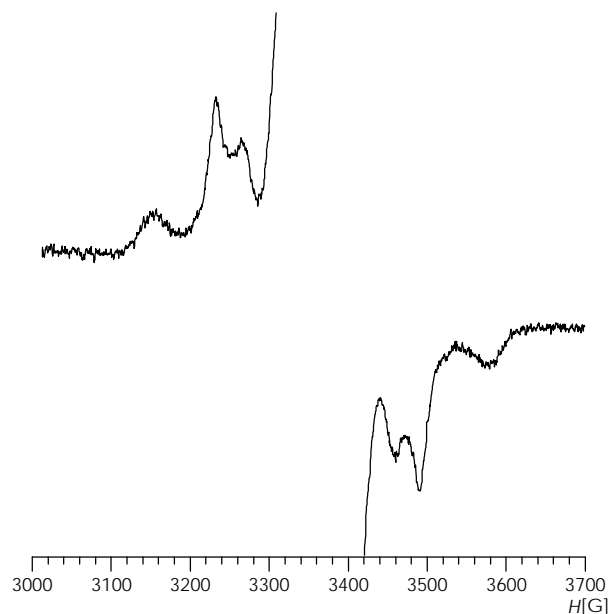
**Fig. 7** UV/Vis spectra of the cocrystal of phenazine and oxalic acid before and after irradiation with light of  $\lambda > 395 \text{ nm}$  in diffuse reflection.— not irradiated, ---- irradiated for 1 s, -.- irradiated for 60 s.

mation is obtained when the spectrum of a cocrystal irradiated for 9 min at  $-94 \text{ }^\circ\text{C}$  is recorded in the range of 3000 to 3700 G. Next to an intense central signal ( $g = 2.00295$ ) the typical signals of a triplet are seen (Figure 9). The zero field parameters are  $|D| = 0.0197 \text{ cm}^{-1}$  and  $|E| = 0.00168 \text{ cm}^{-1}$ . The corresponding  $\Delta M = 2$  transition could not be seen, obviously due to low intensity and low concentration of the triplet species. The zero-field parameters allow the calculation of the average distance of the two triplet electrons on the basis of the two-point model [16]. The calculated distance is 382 pm which is slightly higher than the inter-



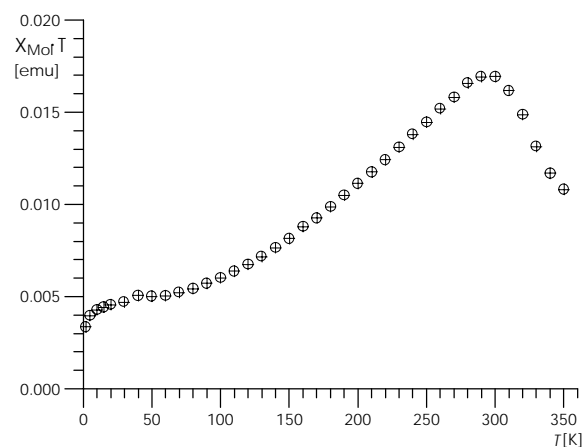
**Fig. 8** E.P.R. spectrum of the irradiated cocrystal of phenazine and oxalic acid as a function of temperature, showing exchange narrowing.

planar distance of two phenazine rings. With rising temperature the intensity of the triplet signal decreases and disappears irreversibly at ca. 60 °C.



**Fig. 9** E.P.R. spectrum of the cocrystal of phenazine and oxalic acid after irradiation at  $-94^\circ$  for 9 min., showing the triplet signal next to the central  $g = 2$  signal.

An interesting result is obtained when a SQUID measurement is carried out on a sample irradiated at room temperature for 9 min and cooled to liquid nitrogen temperature immediately afterwards. A radical concentration of 1.3% is calculated at 40 K from the plot of the product  $\chi_{\text{Mol.}} \cdot T$  versus  $T$  (Figure 10). If the radical concentration does not change with temperature the product  $\chi_{\text{Mol.}} \cdot T$  would remain constant. Figure 10, however, shows an increase of this value, i.e. the number of electrons contributing to the molar susceptibility increases-

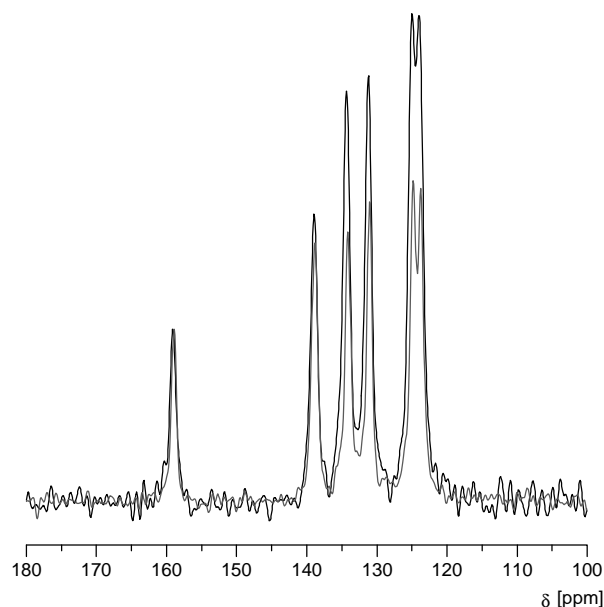


**Fig. 10** Magnetic susceptibility measurement (SQUID) of a cocrystal of phenazine and oxalic acid after irradiation for 9 min ( $\lambda > 360$  nm) as a function of temperature.

es. Such a behaviour is typical for biradicals with a singlet ground-state and a thermally accessible triplet state. In principle, it is possible to calculate from the slope the singlet-triplet energy separation. The situation in our case seems to be more complicated. A triplet state is already populated after irradiation and the increase in molar susceptibility between 40 K and 300 K is not reversible. Above 300 K it decreases, probably due to irreversible destruction of the radicals.

Further information is obtained from solid-state  $^{13}\text{C}$  CP/MAS NMR spectra of an original and an irradiated cocrystal (Figure 11). The asymmetric unit contains seven inequivalent C positions. In the NMR experiment, six resonances are resolved and can be assigned to oxalic acid (158.0 ppm), to the quaternary carbon atoms (139.0 ppm), and to those having attached a hydrogen atom (124.0, 125.0, 131.3, 134.3 ppm) in the phenazine molecule.

If oxalic acid is assumed to be unaffected by irradiation then the resonance at 159 ppm can be used as internal reference for the comparison of the original and irradiated sample. Relative to this signal, the signals of the carbon atoms with hydrogen decrease in intensity by approximately 25%. A possible interpretation of this change is the formation of radicals which cause line shifts and, in particular, significant line broadening. The magnitude of this effect is strongly distance-dependent (proportional to  $1/r^3$  with  $r$  being the distance between the unpaired electron and the nucleus) and can lead to non-observability of nuclei close to radical centers. This would lead to a decrease of intensity in the NMR spectrum which suggests that unpaired electrons reside on



**Fig. 11** Solid state  $^{13}\text{C}$  CP/MAS NMR spectra of the cocrystal of phenazine and oxalic acid before (top) and after irradiation (bottom).

phenazine molecules. It is expected that only a part of the phenazine molecules is affected, but the NMR spectrum can not provide a reliable quantitation of this effect.

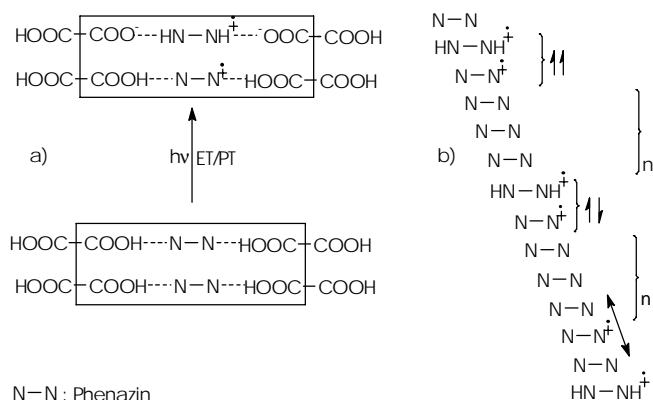
## Discussion

The 1:1 cocrystals of phenazine and fumaric acid, dihydroxyfumaric acid, and oxalic acid are characterized by strong O-H...N and weak C(sp<sup>2</sup>)-H...O hydrogen bonds. One of the basic questions is, why do the oxalic, fumaric, and 2,3-dihydroxyfumaric acids form cocrystals with phenazine and do not prefer to crystallize alone as a neat substance? The intermolecular O-H...O bridges formed by carboxylic acids are known to be the strongest amongst all hydrogen bridges and thus the lattice energy should be sufficiently favourable to form the pure crystals. O-H...N hydrogen bonds are essentially weaker and consequently their contribution to the total lattice energy must be smaller in the cocrystals. However, the sum of the much weaker C-H...O bonds must play a significant role in the stabilisation of the crystal lattices of the cocrystals and consequently their contribution should not be underestimated. Unfortunately, lattice energy calculations are not accurate enough to present a good estimate whether cocrystals are formed or not, even if the overall packing motif is correctly described. In the cocrystals an arrangement is found in which each kind of molecule forms staples surrounded by staples of the other molecule. These structures are different from those reported for cocrystals of phenazine and aromatic carboxylic acids [7]. The carboxylic groups are coplanar, leading to a two dimensional pattern of acid and phenazine units which is largely responsible for the observed crystal structure. A different arrangement had been obtained when phenazine was cocrystallized with *meso*-1,2-diphenyl-1,2-ethanediol [4]. Due to the position of the hydroxy groups in the latter case a ladder-like and not a linear network had been the consequence. While the carboxy groups in oxalic acid are directly linked, there is a CC double bond as spacer in the two other cases. The presence of the double-bond spacer leads to a remarkable difference in the relative position of phenazine molecules in the staples. There is almost no overlap of the  $\pi$ -electron systems of phenazine molecules in the cocrystals with fumaric acid and dihydroxyfumaric acid, – the separation of the "pyrazine" centroids is ca. 530 pm. There exists, however, considerable overlap of the phenazine  $\pi$  systems in the cocrystal with oxalic acid, where the separation of the "pyrazine" centroids is 385 pm. The macroscopic behaviour of the cocrystals seems to be the direct consequence of this different arrangement underlining the importance of the relative position of components in if novel properties are envisioned.

The properties of the cocrystal of oxalic acid with phenazine need to be rationalized. It was found for the cocrystal of phenazine with *meso*-1,2-diphenyl-1,2-ethanediol that a cooperative electron-proton transfer which is thermally reversible can explain the observed photochromism [4]. The primary event on irradiation of the cocrystal of phenazine and oxalic acid seems to be due to a similar electron transfer process. However, it is thermally not reversible and there are features which are different from those of the cocrystal with the diol. A case which can contribute to the understanding of the phenomena is given by the solid state properties of 10-alkylphenazin-5(10*H*)-yl radicals [17, 18]. The X-ray structure shows that some of the radicals form dimers with a separation of ca. 325 pm of the ring planes. An almost perfect  $\pi$ -stacking is encountered. These complexes are called  $\pi$ -mers. Interestingly, the unpaired electrons in these complexes form a singlet. Electronic excitation within the dimers leads to a strong absorption at 855 nm, very similar to the band observed in the cocrystal of phenazine and oxalic acid after irradiation. In solution this absorption does not exist. A second band which is comparable to the 600 nm absorption of the cocrystal (Figure 7) is present in these radicals at 590 nm, in solution it is shifted to 550 nm. It must be related to excitation within a single isolated phenazinyl radical. The e.s.r. spectroscopic investigation in the solid state shows that the singlet biradical is the ground state, that, however, the triplet state is in thermal equilibrium with the ground state.

A model which evolves from our experimental findings and the comparison with the phenazinyl radicals is proposed in Figure 12. Starting point is a light induced electron transfer by irradiation with a cut-off filter Schott GG 395 nm. The singlet radical cation/radical anion pair initially formed, presumably is stabilized by proton transfer from the carboxy group of oxalic acid to the nitrogen atoms of phenazine in the radical anion, similar to what was observed for the cocrystal of phenazine and *meso*-1,2-diphenyl-1,2-ethanediol [4]. The absorption band at 860 nm, attributed in the case of the phenazinyl radicals as due to excitation of electrons in the singlet  $\pi$ -mer, suggests the presence of singlet biradicals. The e.s.r. experiments, however, indicate that a major part of the unpaired electrons in radical ions behaves independently, giving rise to the strong central e.s.r. signal. Some of the singlet biradicals are converted to triplet states as evidenced by the e.s.r. experiment. The triplet electrons reside on neighbouring phenazine units. The SQUID experiment indicates that the number of magnetically active electrons increases with temperature suggesting that some biradicals mutate to two independent, magnetically active electrons. In comparison to the total number of phenazine molecules in the crystal only a small fraction is converted to radical ions.

Thus within a staple of phenazine molecules a biradical might transform to non interacting electrons when electrons or holes move along a staple as proposed in Figure 12.



**Fig. 12** Model for the light induced processes in the cocrystal of phenazine and oxalic acid; a) radical-ion pair generation by a light induced electron-proton transfer; b) schematic re. p.resentation of singlet – and triplet radical ion pairs on neighbouring phenazine molecules, and of the migration of electron holes in the phenazine staple.

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## Experimental

Instrumentation: IR: BIO-RAD FT-IR 135;  $^1\text{H-NMR}$ : Gemini 200;  $^{13}\text{C-CP/MAS}$ : Bruker DMX 300, 75.47 MHz; spinning frequency (MAS): 8.5 kHz; 3.75  $\mu\text{s}$   $^1\text{H}$  90° pulse, 7 ms contact pulse, 320–600 transients with 30s recycle delay; E.S.R.: Bruker ER 420; UV/Vis: J&M TIDAS; (molar ratio of KBr and supramolecule 1 :  $5 \times 10^{-3}$  or pure cocrystal on KBr); Irradiation: 1 kW Hg/Xe lamp (Schott UG5 and GG395 filters).

Chemicals: All chemicals were commercially available.

## Preparation and Characterization of Cocrystals

**Phenazine/fumaric acid:** The cocrystal was grown from a hot saturated solution of an equimolar mixture in acetone. Yellow needles, *m.p.* 196–204 °C – IR (KBr):  $\bar{\nu}/\text{cm}^{-1}$  = 3326 (O-H), 1707 (C=O). – UV/Vis (KBr):  $\lambda_{\text{max}}/\text{nm}$  (abs.) = 254 (0.83), 379 (0.87), 408 (0.79), 430 (0.80). **Phenazine/2,3-dihydroxyfumaric acid:** The cocrystal was grown from a hot saturated solution of an equimolar mixture in acetone. Yellow/orange needles, *m.p.* decomposition >150 °C. – IR (KBr):  $\bar{\nu}/\text{cm}^{-1}$  = 3070 (=C-H), 1850, 1644 (C=O) – UV/Vis (KBr):  $\lambda_{\text{max}}/\text{nm}$  (Abs.) = 256 (0.49), 282 (0.50), 320 (0.59), 382 (0.56), 409 (0.54), 430 (0.54). **Phenazine/oxalic acid:** The cocrystal was grown from a hot saturated solution of an equimolar mixture

in acetone. Small yellow needles, *m.p.* 223 °C. – IR (KBr):  $\bar{\nu}/\text{cm}^{-1}$  = 1726 (C=O). – UV/Vis (KBr):  $\lambda_{\text{max}}/\text{nm}$  (Abs.) = 252 (0.40), 280 (0.50), 324 (0.47), 377 (0.62), 436 (0.70).

**Crystal Data [19]:** Structure determinations were performed with Siemens(Bruker) AXS Smart System at room temperature and Mo-K $\alpha$ -radiation, using Siemens(Bruker) SHELX-TL 5.03 software suite with SADABS absorption correction. The hydrogen atom positions were calculated for ideal positions except of the hydroxy hydrogen atoms, which were located from a difference fourier map and refined as riding groups. They were given isotropic displacement parameters which correspond to the 1.2 fold of the anisotropic equivalent of the attached atoms.

**Phenazine · fumaric acid,**  $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{C}_4\text{H}_4\text{O}_4$ : crystal size 0.25 × 0.22 × 0.05 mm, yellow, monoclinic space group  $P2_1/c$  (Nr. 14),  $Z = 2$ ,  $a = 534.28(3)$ ,  $b = 877.84(5)$ ,  $c = 1499.28(9)$  pm,  $\beta = 98.950(1)^\circ$ ,  $V = 694.62(7) \times 10^6$  pm $^3$ ,  $\rho = 1.417$  gcm $^{-3}$ ,  $\Theta_{\text{max}} = 24.12^\circ$ , intensities measured: 2267, independent: 968 ( $R_{\text{int}} = 0.0115$ ), of which 850 with  $I > 2\sigma(I)$ , max/min transmission 1.00/0.76, 102 parameters,  $R1 = 0.0472$ ,  $wR2$  (all data) = 0.1294,  $\text{Gof} = 1.090$ , residual electron density +0.307/–0.180 eÅ $^{-3}$ .

**Phenazine 1,2-dihydroxyfumaric acid:**  $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{C}_4\text{H}_4\text{O}_6$ : crystal size 0.36 × 0.24 × 0.08 mm, yellow, monoclinic space group  $P2_1/c$  (Nr. 14),  $Z = 2$ ,  $a = 881.38(3)$ ,  $b = 530.64(2)$ ,  $c = 1577.59(5)$  pm,  $\beta = 103.294(1)^\circ$ ,  $V = 718.06(4) \times 10^6$  pm $^3$ ,  $\rho = 1.518$  gcm $^{-3}$ ,  $\Theta_{\text{max}} = 26.39^\circ$ , intensities measured: 5347, independent: 1224 ( $R_{\text{int}} = 0.0255$ ), of which 1013 with  $I > 2\sigma(I)$ , max/min transmission 1.00/0.77, 112 parameters,  $R1 = 0.0592$ ,  $wR2$  (all data) = 0.1567,  $\text{Gof} = 1.062$ , residual electron density +0.560/–0.170 eÅ $^{-3}$ .

**Phenazine · oxalic acid:**  $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{C}_2\text{H}_2\text{O}_4$ : crystal size 0.32 × 0.22 × 0.13 mm, dark green, monoclinic space group  $P2_1/n$  (Nr. 14),  $Z = 2$ ,  $a = 385.51(1)$ ,  $b = 1063.81(2)$ ,  $c = 1470.23(2)$  pm,  $\beta = 95.591(1)^\circ$ ,  $V = 600.09(2) \times 10^6$  pm $^3$ ,  $\rho = 1.496$  gcm $^{-3}$ ,  $\Theta_{\text{max}} = 26.41^\circ$ , intensities measured: 4458, independent: 1045 ( $R_{\text{int}} = 0.0183$ ), of which 878 with  $I > 2\sigma(I)$ , max/min transmission 1.00/0.84, 92 parameters,  $R1 = 0.0494$ ,  $wR2$  (all data) = 0.1431,  $\text{Gof} = 1.085$ , residual electron density +0.338/–0.228 eÅ $^{-3}$ .

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- [19] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications: CCDC-141379 (phenazine-2,3-dihydroxyfumaric acid cocrystal), CCDC-141380 (phenazine-fumaric acid cocrystal), CCDC-141381 (phenazine oxalix acid cocrystal). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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