Supporting Information for

Surface nucleation in solid-state dimerization of nitrosobenzenes promoted by sublimation

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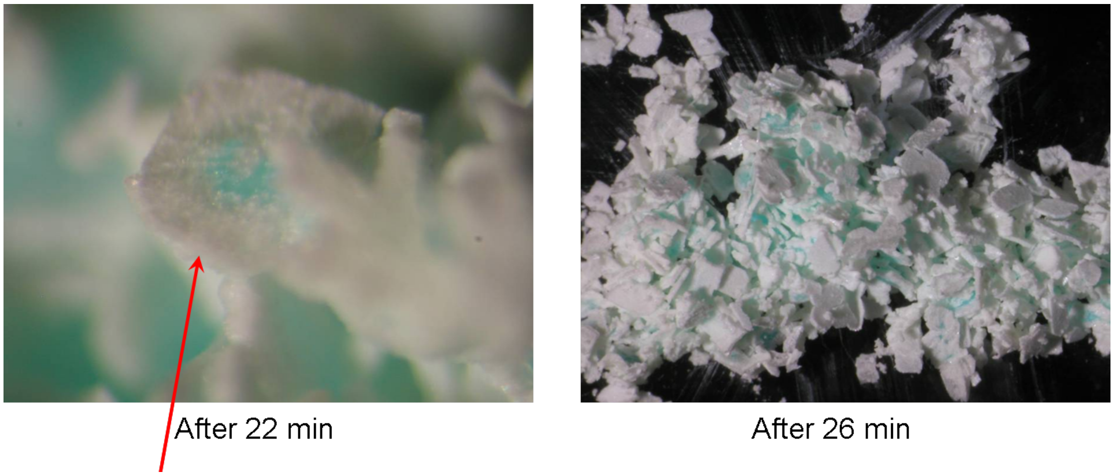
Visual observations



After 22 min

After 26 min

Figure S1. Solid-state dimerization of *p*-chloronitrosobenzene. (left) The arrow indicates crystal growth of the dimer phase which extends to the middle of the surface after having started at crystal edges. (right) In the bunch of crystals, those which are closer to edges of the bunch turn white sooner then those which are in the middle of the bunch. This is probably caused by higher vapour pressure inside the bunch of crystals and thus slower molecule loss by sublimation.

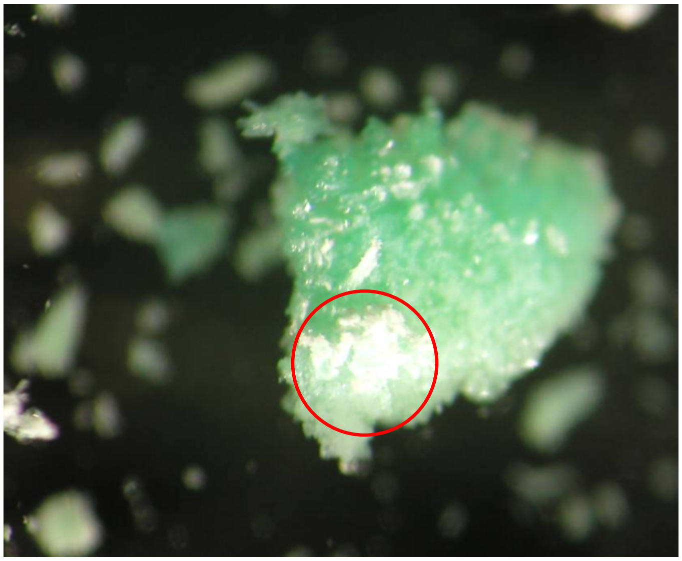


Figure S2. Dimerization reaction in *p*-bromonitrosobenzene after 15 minutes. Circled part of the sample which turned white is exposed to air while the rest of the sample is immersed in glycerol.

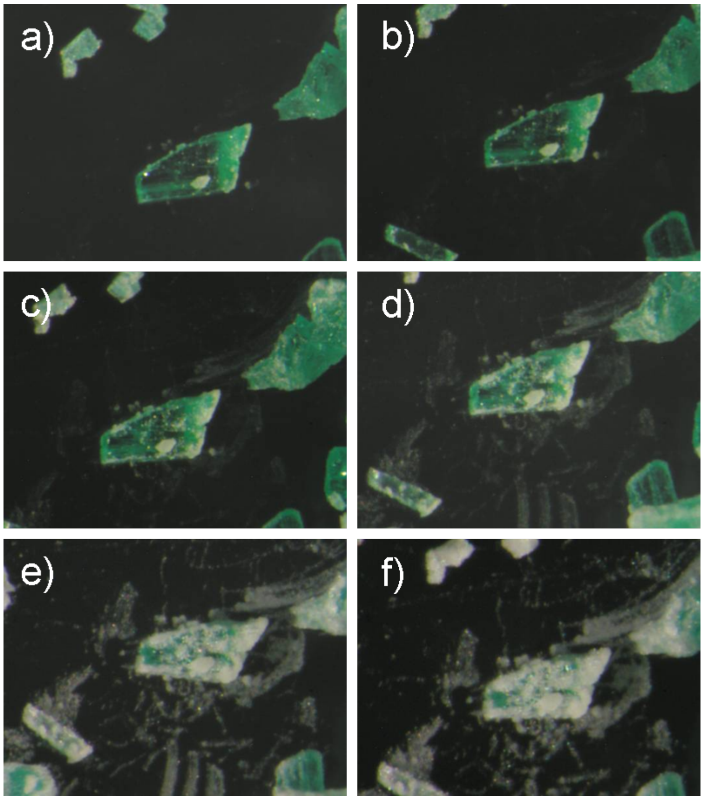


Figure S3. Edge nucleation of the dimer on the crystals of monomeric *p*-bromonistrosonezene after (a) 2 minutes, (b) 4 minutes, (c) 6 minutes, (d) 12 minutes, (e) 90 minutes, (f) 105 minutes.

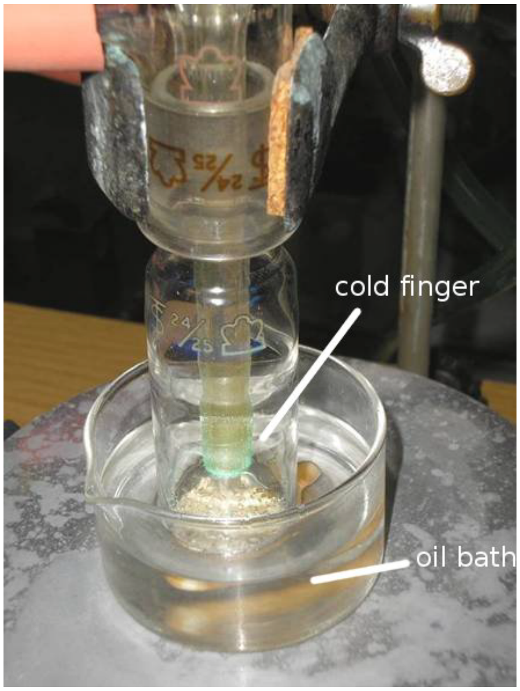


Figure S3. Sublimation apparatus. A green monomer is formed on the cold finger.

DSC and weight loss measurements

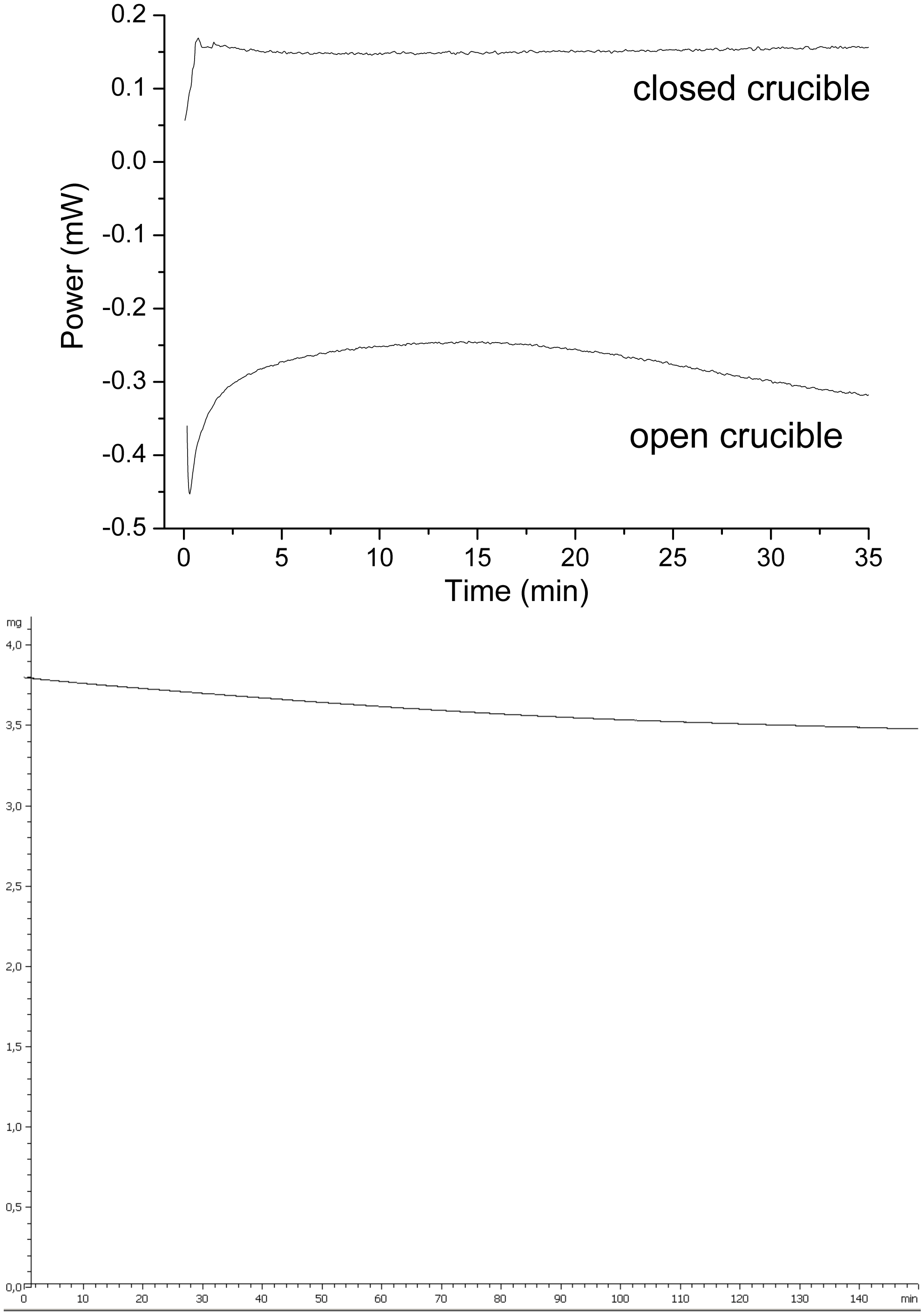


Figure S4. (top) Isothermal DSC thermograms of samples of solid *p*-bromonitrosobenzene undergoing dimerisation in a closed (top) and in an open (bottom) crucible. Exo is up. The crucibles were maintained at constant temperature of 30 ^{o}C. (bottom) Isothermal mass measurement during dimerisation of *p*-bromonitrosobenzene.

Time-resolved powder X-ray diffraction

Time-resolved data for dimerisation of *p*-nitronitrosobenzene were collected on Philips PW 1700 automated diffractometer with control unit PW3710 using the scanning method with the following parameters: Cu *K*α radiation, $2\theta=11°–21°$, continuous scan mode with 0.02° intervals, counting time per interval was 0.25 s, tension of 40 kV and current of 40 mA. With this choice of parameters one measurement cycle lasts 3 min and 20 seconds. The sample was taken from the cold finger of the sublimator and ground in an agate mortar which was previously cooled to –10 °C in a refrigerator in order to slow down the dimerization during grinding. Temperature in the laboratory was 20 °C. Data was collected over a 140 minute period. Data collection was performed with X'pert Software suite 1.2 (*Program package for measuring and analysis of diffraction data on Philips X-ray diffraction equipment*; Analytical, Almelo, the Netherlands, 1999). Background correction and integration of intensities were performed using X'Pert Plus 1.0 (*Program for Crystallography and Rietveld Analysis*; Panalytical, Almelo, the Netherlands 1999).

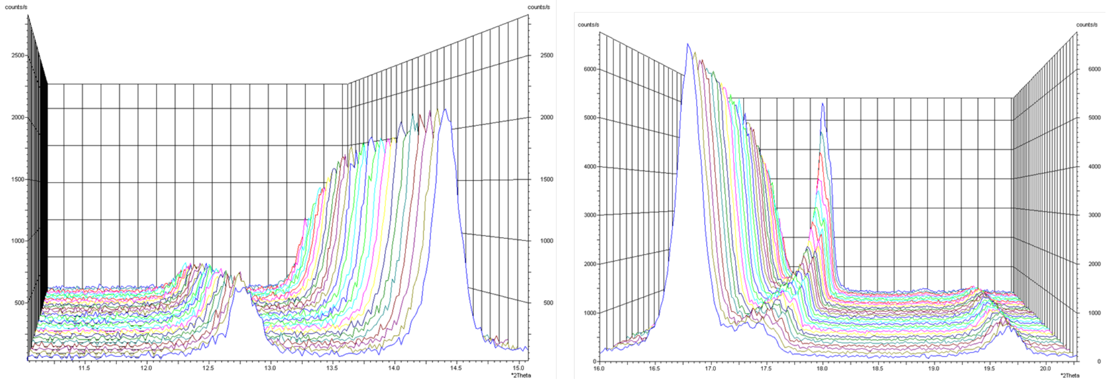


Figure S5. Solid-state dimerization of the *p*-nitronitrosobenzene measured by time-resolved powder X-ray diffraction. The first pattern is in the back, the last in the front. Patterns are separated 3 minutes and 20 seconds in time. (left) 2Theta from 11° to 15° and (right) from 15° to 21°.

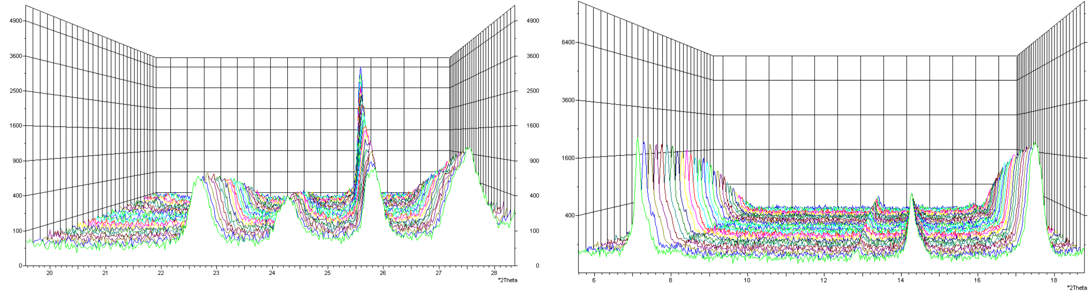


Figure S6. Time-resolved powder diffraction during dimerization of the *p*-bromonitrosobenzene. (left) Patterns form 5° to 19° in 2Theta and (right) form 20° to 29° degrees. First pattern is in the back, last is in the front. Patterns are separated by 10 minutes in time.

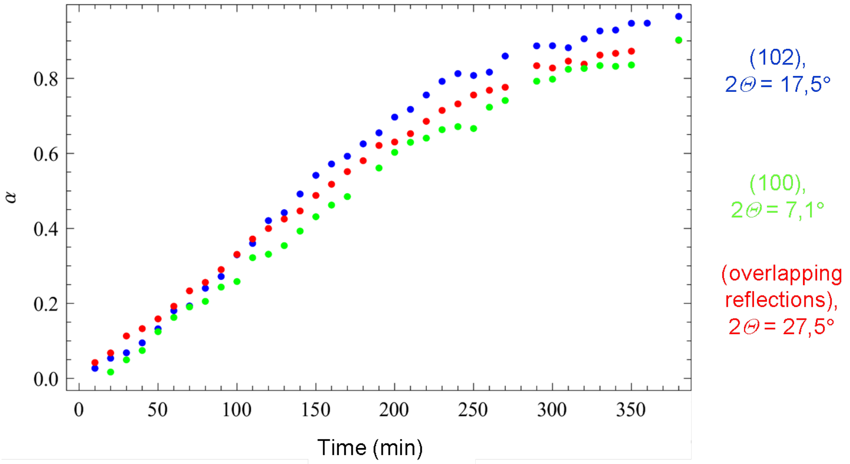


Figure S7. Change in selected reflection intensities during dimerization of *p*-bromonitrosobenzene scaled to the maximum intensity.

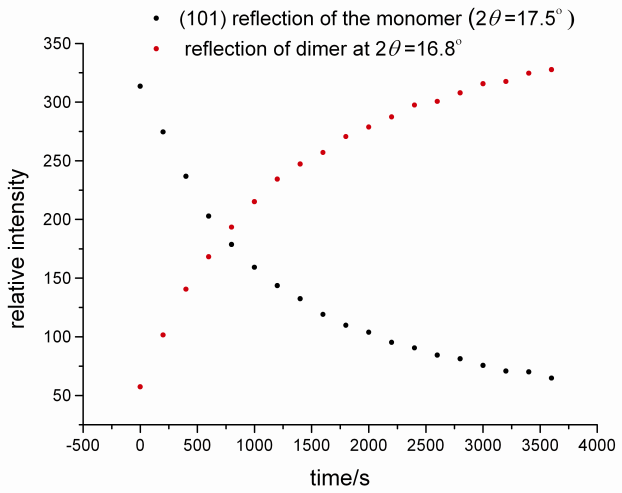


Figure S8. Change in selected reflection intensities of the monomer and of the dimer during dimerization of *p*-nitronitrosobenzene.

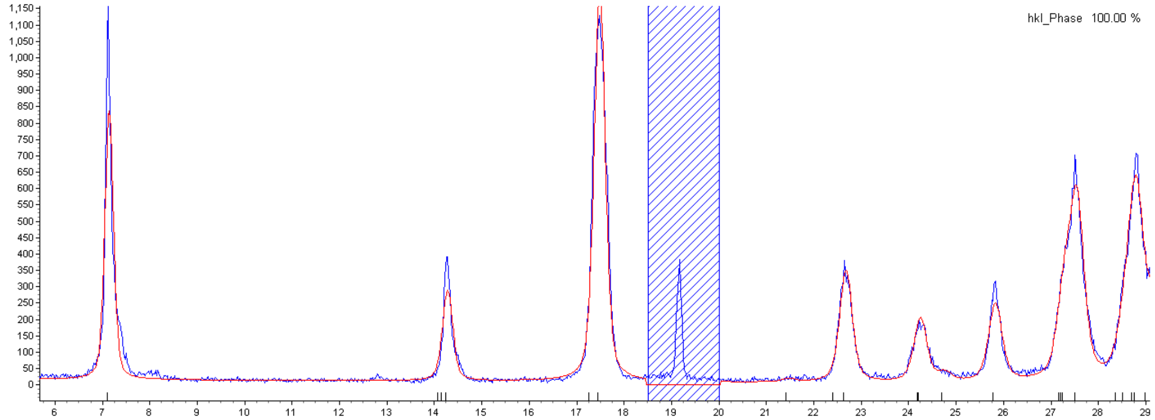


Figure S9. Le Bail fit of the final dimerization product using the unit cell of the dimer of *p*-bromonitrosobenzene. Shaded region is excluded due to an unidentified impurity; this peak did not change in time during the dimerization.

Time-resolved infrared spectroscopy

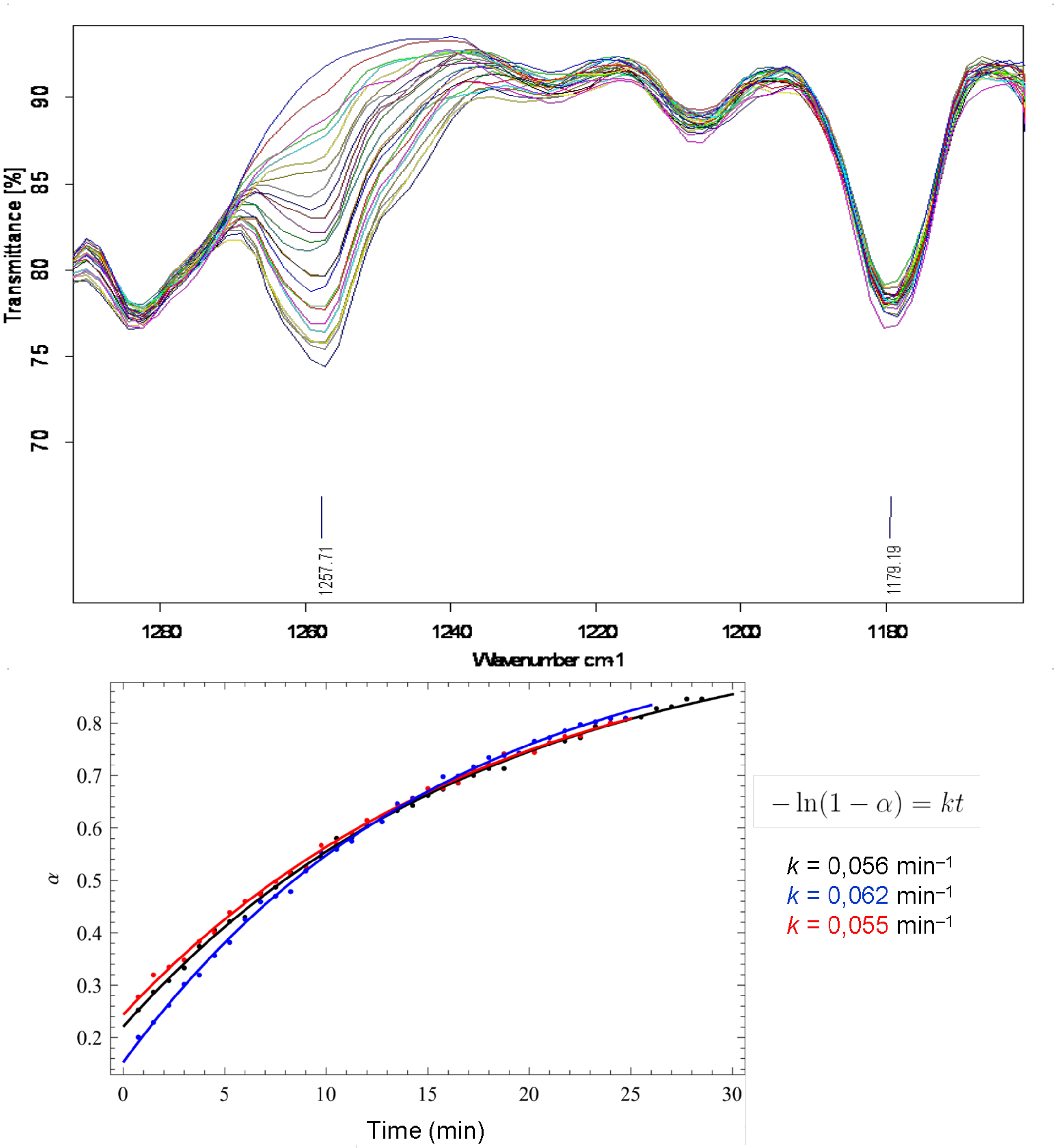


Figure S10. (top) Time-resolved IR spectra of *p*-bromonitrosobenzene. The band at 1258 cm^{-1} belonging to the asymmetric stretching of the ONNO group of the dimer is increasing in intensity. (bottom) Fitting the reaction rate law of the first order to the intensity change of the ONNO stretching of *p*-bromonitrosobenzene from time resolved infrared spectra. Three independent data sets.

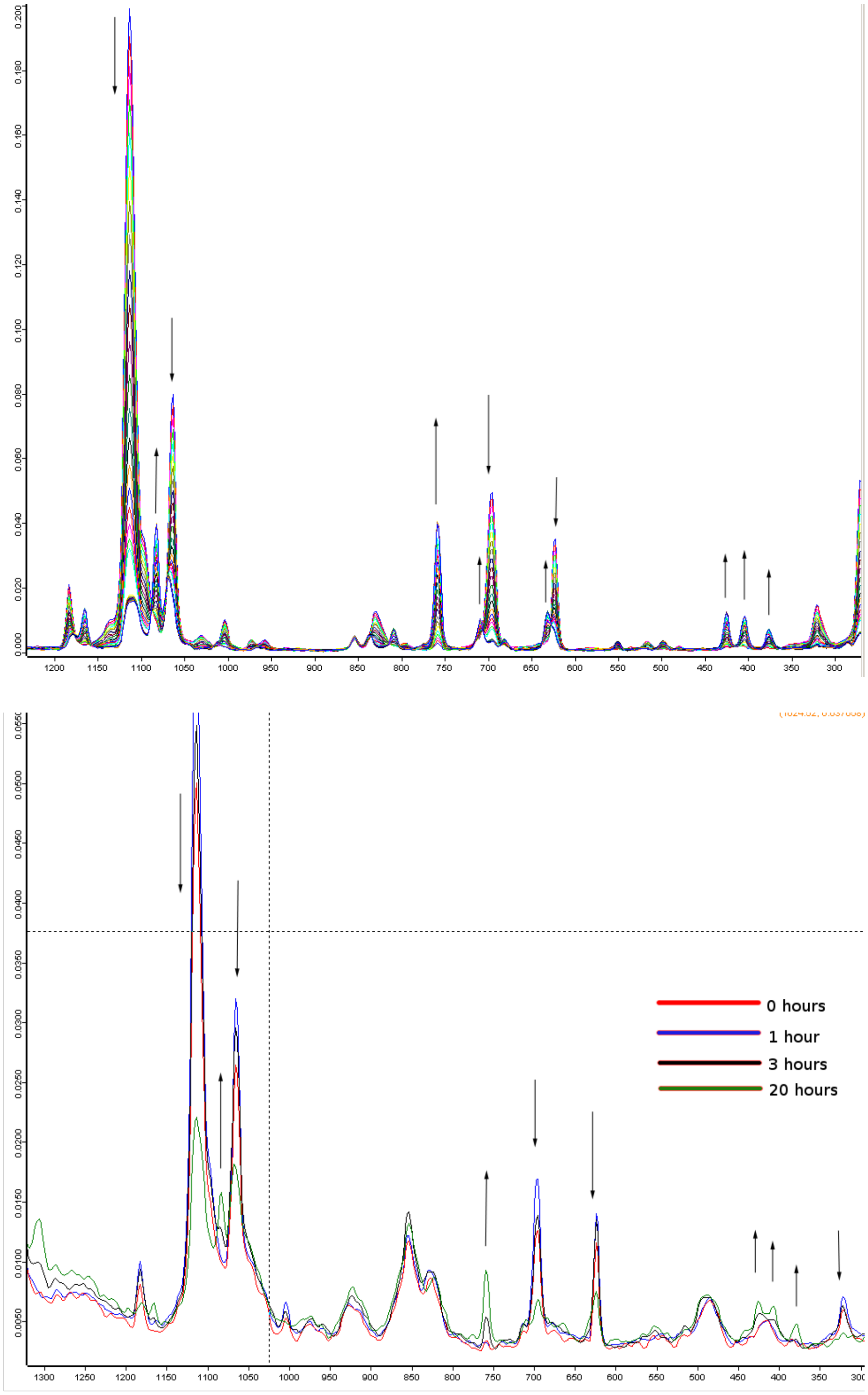


Figure S11. Time resolved Raman spectra of (top) an open sample of *p*-bromonitrosobenzene and (bottom) the sample immersed in glycerol. Spectra of the open sample are separated by three minutes in time. Formation of the dimer is best observable with the line at 758 cm^{-1} since it is not overlapping with monomer bands or with glycerol. Arrows indicate whether the band is increasing or decreasing in intensity.

Single crystal X-ray diffraction

A single crystals of monomeric *p*-nitronitrosobenzene and *p*-chloronitrosobenzene of nitrosobenzene for the single-crystal diffraction experiments were prepared by sublimation of the dimer. Pressure was kept at around 0.1 mbar while the temperature of the dimer was slowly raised from 20 °C to 50 °C. The temperature of cooling water was around 10 °C. After large enough green to blue crystals were formed on the cold finger, sublimation was stopped and single crystals of monomers were glued on the tip of a glass fiber using silicone grease and were quickly mounted on the diffractometer and put in a stream of nitrogen gas at 100 K.

Data were collected by a series of omega-scans on an Oxford Diffraction Xcalibur3 CCD X-ray diffractometer with graphite-monochromated Mo$K\alpha$ radiation and processed using CrysAlis[Red] software package. Crystal structure was solved with direct methods implemented in SHELXS-97 and refined on F^2 by full matrix least squares using SHELXL-97[Shel]. Both programs were used as a part of the WinGX[Far] software package. Crystal structure was refined with restraints on geometrical parameters (DFIX and SAME), temperature factors (ISOR and DELU) and occupancies of the disordered atoms of the nitroso group. Carbons atoms were refined as anisotropic with no restraints. Hydrogen atoms were placed on geometrically calculated positions with C–H bond distance of 0.93 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{C})$ of the C atom to which they were attached. ORTEP3[far2] and Schakal99[kell] were used for graphical presentation of the molecular structure and crystal packing respectively.

Crystal structure of monomeric *p*-nitronitrosobenzene

Crystal structure was solved in $P2_1/n$ space group with half of molecule in the asymmetric unit and two molecules in unit cell. Molecule of *p*-nitronitrosobenzene lies on the centre of symmetry. This imposes orientational disorder which is most probably static in its nature. In addition, the nitroso group is itself disordered as if the molecule is rotated around an axis going through C1 and C1$^{\mathrm{i}}$ (i = $-x, -y, -z$) Occupancies of these two positions of nitroso group refined to 0.29 and 0.21. Such disorder of the whole molecule renders nitroso group in four positions. Molecules of *p*-nitronitrosobenzene are packed in a herringbone motif. Crystal structure of *p*-nitronitrosobenzene is isostructural to the crystal structure of 1,4-dinitrobenzene. In the case of monomeric *p*-bromonitrosobenzene, where molecules are also orientationaly disordered, it was fairly straightforward, based on the topochemical principle, to assume which of the suitably oriented neighbouring molecules could form a dimer within the monomer crystal. With *p*-nitronitrosobenzene it is much more difficult to make a similar assumption. Consider one molecule of the monomer: assuming such orientation of all neighbouring molecules that would the best for dimerization (simplest criteria for selecting such orientation would be the distance between nitrogen atoms of neighbouring nitroso groups), it is difficult to tell which two molecules will form a dimer according to the topochemical principle. It could well be that dimerization occurs between all possible pairs of neighbours. Shortest distances between nitroso groups of the two molecules favourably oriented for dimerization are 3.48 Å and 3.47 Å.

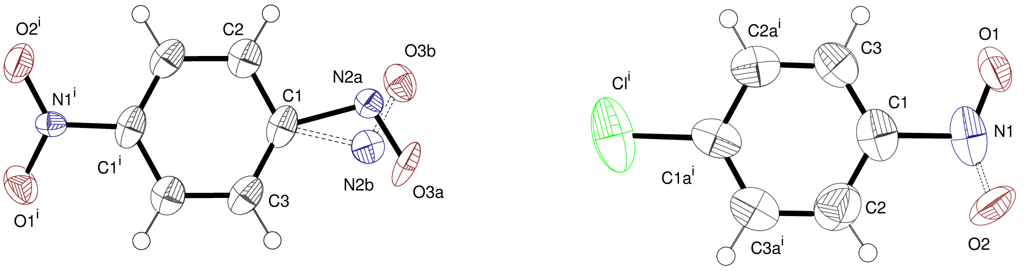


Figure S12. ORTEP representations of molecular structures of (left) *p*-nitronitrosobenzene and (right) *p*-chloronitrosobenzene. Both crystal structures are disordered since the molecules lies on an inversion center thus the molecule having two orientations. In both derivatives the nitroso group is additionally refined in two orientations (dashed lines). In *p*-nitronitrosobenzene the carbon atoms are assigned a single position while they are assigned two positions in the the *p*-chloro crystal structure.

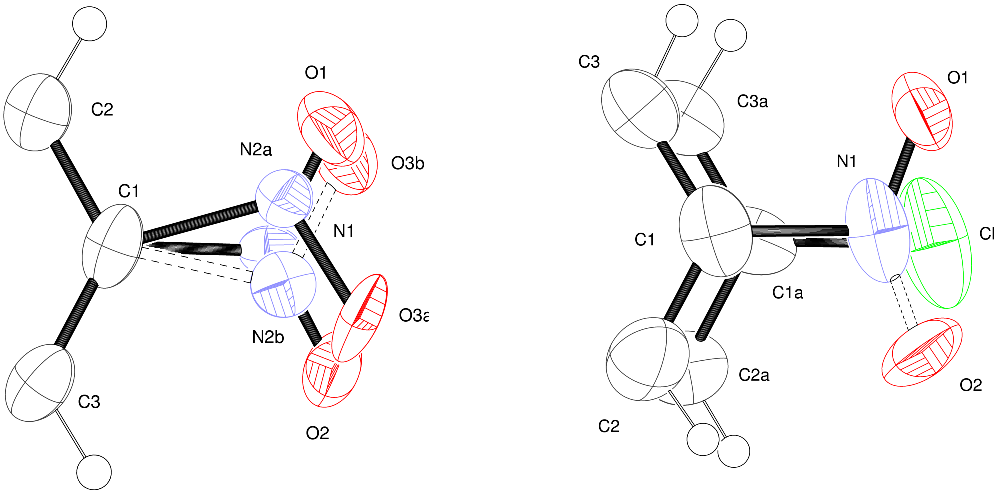


Figure S13. ORTEP representations of asymmetric units of (left) *p*-nitronitrosobenzene and (right) *p*-chloronitrosobenzene.

Crystal structure of monomeric *p*-chloronitrosobenzene

Monomeric *p*-chloronitrosobenzene dimerises in the P21/n space group with the molecules also positioned on an inversion centre. This imposes orientational disorder of the molecule (Fig. 14). Additionally, in each orientation, the nitroso group is distributed over two positions with occupancies of 0.30 and 0.20.

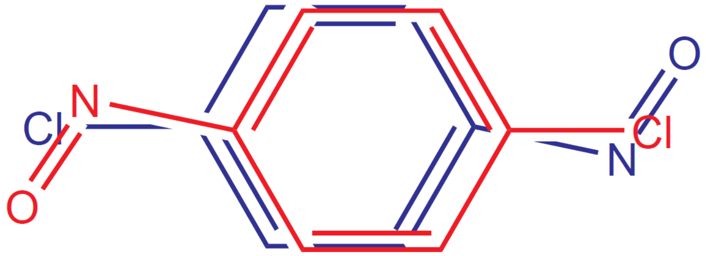


Figure S14. Schematic representations of the two orientation disorder in *p*-chloronitrosobenzene.

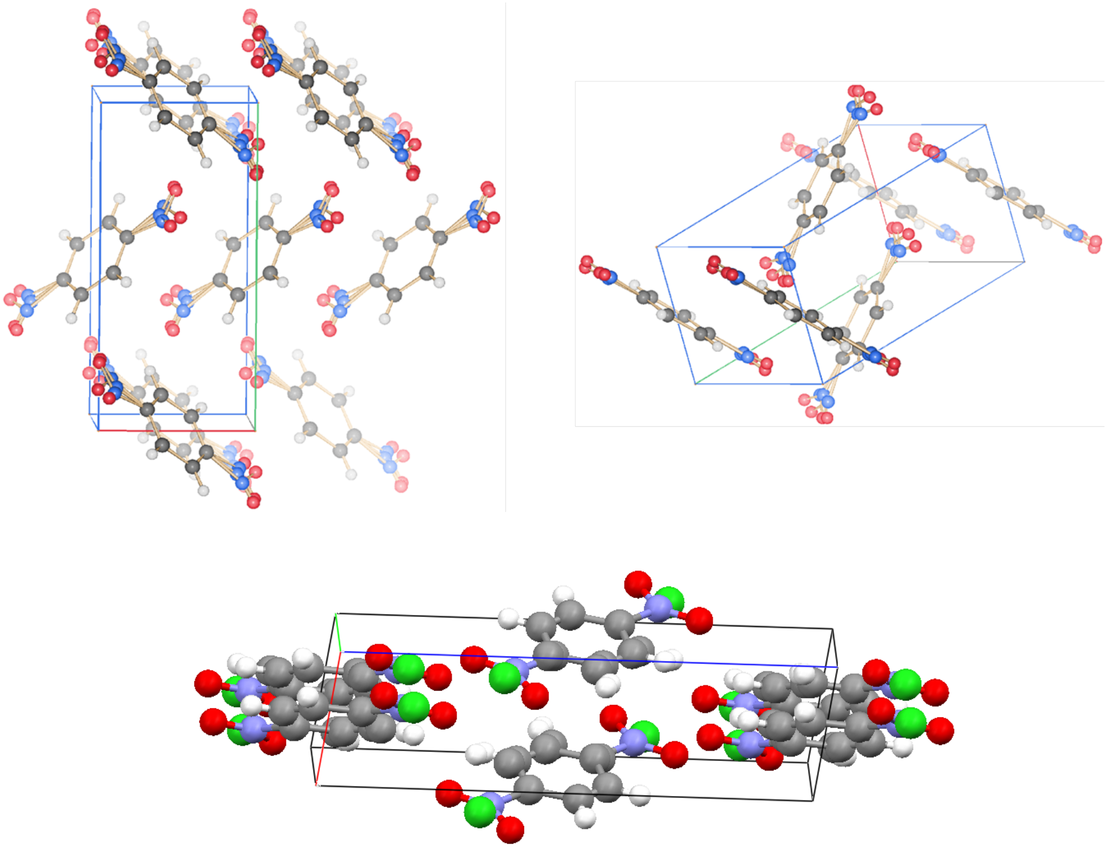


Figure S15. Packing in the crystals of monomeric *p*-nitronitrosobenzene (above) and *p*-chloronitrosobenzene (below).

Sample preparation

***p*-Nitronitrosobenzene** was prepared by oxidation of *p*-nitroaniline with *oxone*® ($K_2SO_5 \times K_2SO_4 \times KHSO_4$). Dichloromethane solution of the amine (10 mmol in 40 ml) was added in portions to the vigorously stirred mixture of DCM (10 ml) and water solution of oxone (20 mmol, 100 ml). The reaction mixture was kept open to the atmosphere. The solution slowly became green indicating the formation of nitroso species. After approximately 1 hour, DCM layer was separated, washed twice with hydrochloric acid (c = 1 mol dm^{-3}, 2×20 ml) and water (20 ml). The solution was dried on anhydrous $CaCl_2$ and the DCM was separated on a rotatory evaporator. The obtained yellow solid was purified by sublimation to yield first the monomeric *p*-nitronitrosobenzene which dimerized within an hour to a white powder.

p-Chloronitrosobenzene was prepared in the same way as *p*-nitronitrosobenzene.

References

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