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Une étude cristallographique: superspace description of a commensurate composite cocrystal of 4,4'-dinitrobiphenyl and biphenyl†

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We report the structure of a 3:1 cocrystal of 4,4'-dinitrobiphenyl and biphenyl. The cocrystal can be regarded as a commensurate column composite crystal and therefore is described in superspace. The structure is monoclinic at 100 K (superspace group $C2(\sigma_1 0 \sigma_3) 0$), but undergoes a single-crystal-to-single-crystal phase transition upon cooling, which results in a triclinic distortion at 20 K ($C1(\sigma_1 \sigma_2 \sigma_3) 0$). Unlike similar symmetry-lowering phase transitions, this transition is not found to induce twinning. Other structurally similar cocrystals with 4,4'-dinitrobiphenyl and small organic molecules have been reported in the literature demonstrating that 4,4'-dinitrobiphenyl is prone to form composite crystals.

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1 Introduction

An incommensurate or a commensurate *composite crystal* is a single thermodynamic phase containing at least two components, each of which is arranged in space according to its own lattice.^{1–4} Sometimes also the term *intergrowth compound* is used to refer to composite crystals.^{5,6}

For two or more different lattices to define a single crystalline phase there are some space-fitting requirements. They follow from the requirement that the unit cell of one component (hereafter denoted as subsystem) must be empty at places where atoms of the other subsystems exist (compare Fig. 1(1) and (2)). Accordingly, two types of composite crystals can be distinguished:⁴ 1) layer composites, and 2) column composites. For the former ones two (or more) subsystems form an interleaved layer structure (see Fig. 1 for schematic examples). The space-fitting requirement for such structures is that c^* vectors of both of the subsystems must be identical (if c^* is the stacking direction of the layers).

The other type of composite crystals — column composites are interleaved columnar structures (see Fig. 2). For such structures the space-fitting requirements are that the vectors a_A^* and a_B^* are identical as well as the vectors b_A^*

and b_B^* and are identical (if the columns are parallel to c). The columns of each subsystem are spatially distributed on a common grid when projected on the a^*b^* plane.

The very essence of composite crystals is that, apart from the space-fitting requirements the lattices of the respective

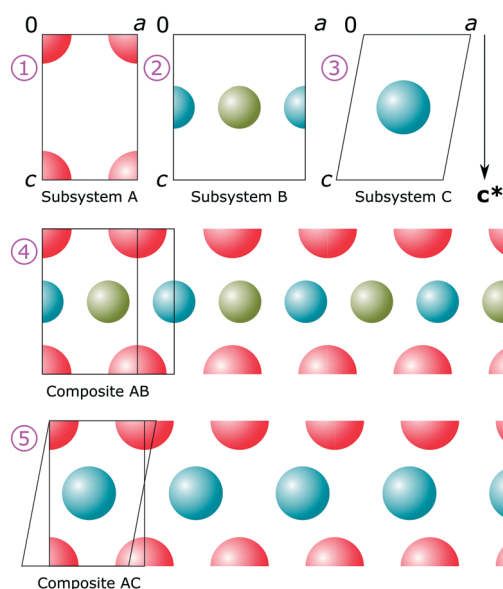


Fig. 1 Schematic representation of incommensurate layer composites. (1–3): The unit cell of one subsystem contains a layer motif (atomic layers parallel to a , b with $a_A \neq a_B$ and $a_A \neq a_C$, but with a_A , a_B , a_C and b in a single plane) and empty space to accommodate a layer from another subsystem. (4 and 5): To fulfill the space-fitting requirement for a layer composite structure it is necessary that both c^* vectors are identical (notice that c^* is perpendicular to a and to b).

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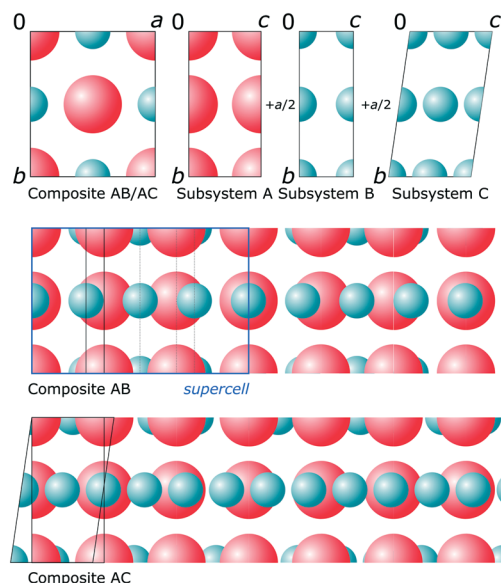


Fig. 2 Schematic representation of a commensurate (AB) and an incommensurate (AC) column composite. Columns are arranged on a common grid on (a, b) to fulfill the space-fitting requirement. The periodicities of both columns along the c axis are generally not commensurate (see AC), but in case they are — a supercell can be chosen to describe the structure in 3-dimensional space (see AB).

subsystems are rationally independent with each other. Composite crystals are usually incommensurate and therefore non-stoichiometric (regarding their constituent components). For incommensurate layer composites the term *misfit layer compound* is frequently used.^{3,7–9}

The structures of incommensurate composite crystals can only be described using the superspace formalism.^{1,2,4} It can happen, however, that supercell lattices can be derived from the respective subsystem lattices so that they match perfectly¹⁰ (see Fig. 2(middle) for an example in which $c_A : c_B$ is a rational number 3 : 4). In that case the composite crystal is commensurate and a conventional 3-dimensional approach can be used to describe its structure with respect to the supercell.¹¹ Nevertheless, the superspace formalism is often beneficial for understanding commensurate composites and commensurately modulated structures in general.^{12–15} For example, transitions to structurally similar but incommensurate phases might be induced by varying temperature and pressure.¹⁰ Consistency in structure descriptions is crucial for understanding solids.

In this study, a commensurate composite 3 : 1 cocrystal of 4,4'-dinitrobiphenyl and biphenyl (Fig. 3) has been described in superspace.

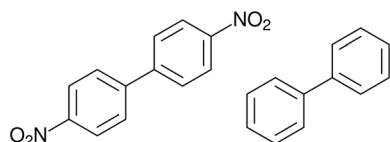


Fig. 3 Molecular formulas of 4,4'-dinitrobiphenyl and biphenyl.

The structure of this two-component compound has been studied in 1948.¹⁶ However, no correct space group nor the atomic positions were derived. Furthermore, similar cocrystals (between 4,4'-dinitrobiphenyl and other biphenyl derivatives) have been studied at that time some of which apparently being incommensurate.^{17–19} We show that the structure of the 4,4'-dinitrobiphenyl and biphenyl cocrystal is monoclinic at 100 K and that there is a single-crystal-to-single-crystal phase transition at a lower temperature resulting in a triclinically distorted structure at 20 K.

2 Experimental section

2.1 Single crystals

4,4'-Dinitrobiphenyl (99%) and biphenyl (99.5%) were purchased from Enamine Ltd. and Sigma-Aldrich, respectively. Single crystals were obtained by slow evaporation from an acetone solution.

2.2 X-ray diffraction data collection

The diffraction data were collected at beamline P24 of PETRA-III at the German Electron Synchrotron (DESY) facility in Hamburg, Germany. A wavelength of 0.5000 Å was used. The data were recorded on a Pilatus 1M CdTe detector. A total of 10 runs (ϕ -scans) were measured. For each run 3620 frames were collected with an exposure time of 0.1 s per 0.1 deg. The runs were binned to a single run and then each consecutive 10 frames were again binned to obtain 362 frames of 10 s exposure per 1 deg rotation. The crystal was measured at 100 and 20 K.

2.3 Data integration

CrysAlisPro 39.46 software²⁰ was used for data integration. Empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm, was applied.

2.4 Structure refinement

The structure at 100 K was solved for the supercell in $C2$, employing SUPERFLIP software.²¹ Structure refinements were performed with JANA2006.²² Based on the 3D model, a refinement in $(3 + 1)D$ was set up and refined. For hydrogen atoms the riding model was used in the refinements.

The $(3 + 1)D$ model was then used for the data measured at 20 K. The R_1 converged to a value of 0.0965, which seemed to be unsatisfactory. Triclinic distortion of the monoclinic lattice with possible twinning was considered. The data were averaged according to the Laue class $\bar{1}$, the contents of the asymmetric unit were doubled using a 2-fold rotation symmetry along the former monoclinic axis and then refined as triclinic. The R_1 value decreased to 0.0479.

3 Results and discussion

3.1 Structures of the cocrystal phases

4,4'-Dinitrobiphenyl and biphenyl forms a 3:1 cocrystal that is a commensurate composite crystal. At 100 K, the unit cells of both subsystems are monoclinic and the superspace group of the composite crystal is $C2(\sigma_1 0 \sigma_3)0$ (see Table 1 for structural and refinement data). Subsystem A contains half a 4,4'-dinitrobiphenyl molecule in the asymmetric unit and subsystem B contains half a biphenyl molecule in the

Table 1 Crystallographic data for the structures of 4,4'-dinitrobiphenyl: biphenyl 3:1 cocrystal phases (obs. reflections: $[F^2 > 3\sigma(F^2)]$)

Crystal data		
<i>T</i> /K	100	20
Formula	$3(C_6H_8N_2O_4) \cdot C_{10}H_{10}$	
Crystal system	Monoclinic	Triclinic
Superspace group	$C2(\sigma_1 0 \sigma_3)0$	$C1(\sigma_1 \sigma_2 \sigma_3)0$
<i>q</i>	(0, 0, 1/3)	(0, 0, 1/3)
<i>t</i> ₀	0	0
Subsystem A		
<i>a</i> /Å	19.7947(4)	19.7858(8)
<i>b</i> /Å	9.4219(2)	9.3970(5)
<i>c</i> /Å	3.5826(1)	3.5684(2)
<i>α</i> /°	90	89.986(4)
<i>β</i> /°	98.7506(16)	98.729(4)
<i>γ</i> /°	90	89.982(4)
<i>V</i> _A /Å ³	660.39(3)	655.78(6)
<i>Z</i> _A , <i>Z</i> _A *	2, 0.5	2, 1
Subsystem B		
<i>W</i>	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$
<i>V</i> _B /Å ³	3 <i>V</i> _A	3 <i>V</i> _A
<i>Z</i> _B , <i>Z</i> _B *	2, 0.5	2, 1
<i>F</i> (000)	307	307
<i>D</i> _x /g cm ⁻³	0.8709	0.8770
<i>μ</i> /mm	0.031	0.032
Data processing		
Laue class	2/ <i>m</i>	$\bar{1}$
<i>R</i> _{int} (obs.)	0.0661	0.0547
No. of refl.	19 670	16 663
No. of unique refl.	4533	8018
No. of obs. refl.	4021	7100
Resolution limit/Å ⁻¹	0.65	0.65
Refinement		
Refinement method	Full-matrix least-squares on <i>F</i>	
<i>R</i> ₁ (obs.)	0.0539	0.0479
<i>R</i> _{<i>m</i>=0} (obs.)	0.0551	0.0484
<i>R</i> _{<i>m</i>=±1} (obs.)	0.0527	0.0475
w <i>R</i> (all)	0.0734	0.0625
No. of parameters	243	483
H-Atom treatment	Constr.	Constr.
Weighting scheme	$w = 1/(\sigma^2(F) + 0.0001F^2)$	
$\Delta\rho_{\max}/e \text{ \AA}^{-3}$	0.32	0.45
$\Delta\rho_{\min}/e \text{ \AA}^{-3}$	-0.20	-0.34

asymmetric unit. The 4,4'-dinitrobiphenyl molecules are stacked face-to-face forming infinite columns, while the biphenyl molecules form infinite chains with the long molecular axis approximately parallel to the chain direction, *i.e.* *c*-axis (see Fig. 4).

For column composites one-dimensional modulations can occur in each of the sublattices due to interlattice interaction perturbations.² For the studied 4,4'-dinitrobiphenyl: biphenyl cocrystal a commensurate modulation in 4,4'-dinitrobiphenyl stacks is present (see Fig. 5). There is a significant displacement of the molecule along the *a*-axis. This can be summarized in a *t*-plot depicted in Fig. 6. For the rest of the 4,4'-dinitrobiphenyl atoms the corresponding *t*-plots are very similar as there is no major variation in molecular conformation. The conformation of the 4,4'-dinitrobiphenyl molecule can be described with two torsion angles — one between the two phenyl rings, and the other one between the NO₂ group and the phenyl ring (even though there are two NO₂ groups, the molecule has a 2-fold rotation symmetry coinciding with the respective symmetry operator of the (super)space group, *i.e.* *Z'* = 0.5). These torsion angle values are listed in Table 2. Regarding the biphenyl molecule, there is a small deviation from planarity with the torsion angle between the phenyl rings being 1.3(5)°.

The superspace approach allows to use fewer refinement parameters. In the supercell, there are 33 non-hydrogen atoms present and each of them requires 3 positional and 6 anisotropic displacement parameters (ADPs) which totals 297 refinable parameters. In the (3 + 1)-dimensional structure description, the atomic positions and the anisotropic displacement are described using a set of basic parameters and parametrized modulation functions. The maximum number of parameters, which does not cause singularity during the refinement, is the same for such a commensurate

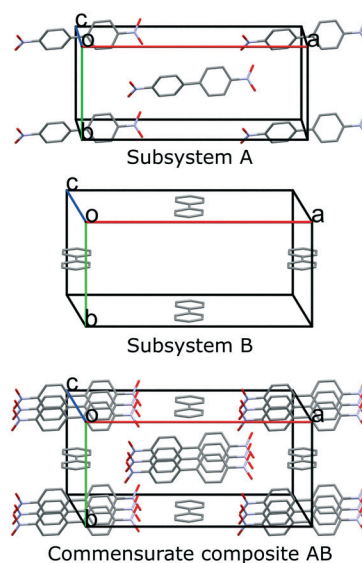


Fig. 4 Unit cells of both subsystems and the supercell of the commensurate composite cocrystal.

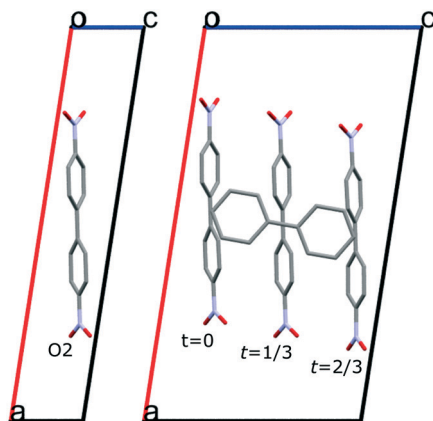


Fig. 5 Basic cell of subsystem A (4,4'-dinitrophenyl) and the supercell of the commensurate composite cocrystal showing a positional modulation of the 4,4'-dinitrophenyl molecules caused by interlattice interaction perturbations.

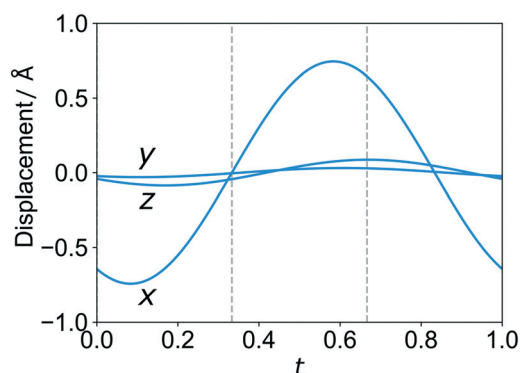


Fig. 6 t -Plot of atom O2 displacement (commensurate t sections indicated with dashed lines). The largest displacement from the basic position is present for coordinate x , while the modulation of coordinates y and z is small.

case. However, *e.g.* the anisotropic displacement modulation functions can be fitted with fewer parameters still resulting in a good description of the electron density. Moreover, such a description is still physically meaningful and sensible. By using a smaller number of ADPs, it was possible to reduce the number of parameters to 243 from the 297 \ddagger required to describe the supercell in 3-dimensional space. Using all the allowed parameters to describe the anisotropic displacement surely reduces the R_1 value, however, this reduction is insignificant (from 0.0539 to 0.0516). Another benefit of the superspace approach is that for each parameter and average value, referring to the basic structure, is refined in conjunction with modulation parameters. The latter are usually small thus making the refinement more stable.

As mentioned in the Introduction section, the room temperature (supercell) structure of this cocrystal has been

\ddagger In both cases an additional parameter is needed to refine the scale, but the parameter y for one atom needs to be fixed to fix the origin for the (super)space group $C2$ or $C2(\sigma_1\sigma_3)0$.

Table 2 Torsion angles defining conformation of the 4,4'-dinitrophenyl molecule in the monoclinic and triclinic phase (* — in the monoclinic phase, the torsion angles are related by symmetry to the row above)

Torsion/ $^\circ$	Monoclinic			Triclinic		
	$t = 0$	$t = 1/3$	$t = 2/3$	$t = 0$	$t = 1/3$	$t = 2/3$
Ph-Ph	-35.0(3)	-36.0(3)	-35.0(3)	-32.6(3)	-36.2(3)	-36.4(3)
Ph-NO ₂	-10.8(3)	-11.4(3)	-3.5(3)	-10.9(4)	-12.2(4)	-3.5(4)
Ph-NO ₂ *	-10.8(3)	-11.4(3)	-3.5(3)	-11.0(4)	-12.0(4)	-3.6(4)

studied in the early days of crystallography.¹⁶ No atomic positions were provided and the space group was concluded to be Cm . Our present structural study shows that there are no mirror planes present, *i.e.* the true space group of the supercell is $C2$. A structure with mirror symmetry elements would be spatially possible, but in that case all the molecules were completely planar (with the discussed torsion angles of the biphenyl and 4,4'-dinitrophenyl molecules being 0°).

Furthermore, we discovered that there is a single-crystal-to-single-crystal phase transition occurring upon cooling for this material. At 20 K the structure is a triclinic distortion of the above described monoclinic phase (superspace group $C1(\sigma_1\sigma_2\sigma_3)0$, see Table 1). The distortion affects the 4,4'-dinitrophenyl molecules for which there is no longer 2-fold rotational symmetry imposed by the (super)space group. The corresponding phenyl-NO₂ torsion angles are slightly different in the triclinic phase (see Table 2). Furthermore, the triclinic symmetry is corroborated by decrease in R_1 value from 0.0965 to 0.0479 for the monoclinic and triclinic refinements of the 20 K data, respectively. Moreover, α and γ angles are significantly distorted from the monoclinic symmetry (see Table 1).

Lowering of symmetry at low temperatures without major reorganization of the atomic arrangement has long been known. Usually it is accompanied with pseudomerohedral twinning. The twin volume fractions are often equal due to the probabilistic nature of the mechanism behind such a phase transition. Some mechanical factors may cause deviations from the 0.5:0.5 twin volume ratio. In this case, the refinement of the twin volume fraction of the second domain ($twvol2$; with $twvol1 = 1 - twvol2$) soon reached a value close to 0 and was unstable. It indicates that by chance only one of the two possible twin domains occurred or its volume fraction is so close to unity that it is impossible to quantify the ratio reliably.

3.2 Other similar cocrystals

4,4'-Dinitrophenyl is prone to form structurally similar cocrystals with several substituted biphenyls and urea. The cocrystal with urea (refcode in CSD: BAFWIO) has a stoichiometry of 1:1, it crystallizes in $P2_12_12_1$ and is referred to as clathrate.²³ The organization of the structure is nevertheless identical to the 3:1 cocrystal of 4,4'-dinitrophenyl and biphenyl.

Furthermore, there is a 3:1 cocrystal of 4,4'-dinitrophenyl and 4-hydroxybiphenyl (CIMCIK), for which

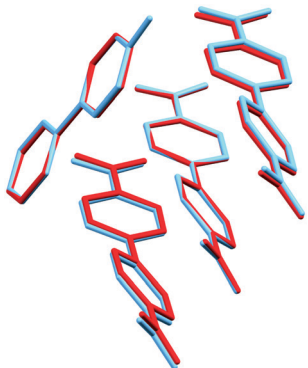


Fig. 7 Best overlay of the asymmetric units of the 4,4'-dinitrophenyl – biphenyl (red) and 4,4'-dinitrophenyl – 4-hydroxybiphenyl (blue) cocrystal triclinic supercells.

the structure is even more similar to the presently studied material.^{17,24} In the original study from 1946, monoclinic symmetry was considered and the structure was reportedly solved in space group *Cm*.¹⁷ Around 40 years later this structure was redetermined to show that there is no mirror plane present as the 4,4'-dinitrophenyl molecules are twisted and not planar. Furthermore, the redetermined structure is reported as triclinic and treated in a primitive unit cell (space group *P1*).²⁴ The corresponding *C*-centered unit cell is nearly monoclinic with α and γ angles of $90.15(2)^\circ$ and $90.20(2)^\circ$, respectively. This is consistent with the observed triclinic distortion of the 4,4'-dinitrophenyl – biphenyl cocrystal at low temperature presented in this study. The best overlay of the asymmetric units of the triclinic supercells are depicted in Fig. 7.

In addition, there are 5 other cocrystals with biphenyl derivatives reported having identical structural organization that can be regarded as composite crystals. Those are 4,4'-dinitrophenyl cocrystals with benzidine, *N,N,N',N'*-tetramethylbenzidine, 4,4'-dihydroxybiphenyl, 4-iodobiphenyl, and 4-bromobiphenyl.¹⁸ The stoichiometries vary according to the guest component molecule length (1:3, 1:4, 2:7). Cocrystals with 4-iodobiphenyl and 4-bromobiphenyl apparently feature incommensurate modulations and could be one of the first organic aperiodic crystals ever reported.¹⁵ Structural modulation was, of course, not recognized in the original work due to the concept of aperiodic crystallography not being formulated by the time. The diffraction patterns with satellite reflections were referred to demonstrating 'periodic errors in the crystal lattice'.¹⁹

4 Conclusions

4,4'-Dinitrophenyl forms a cocrystal with biphenyl that can be regarded as a composite crystal and thus described in superspace. The molecule is prone to form structurally similar composite crystals with several other molecules among which there are substituted biphenyls and urea. The diverse variety of guest molecules that can fill the isostructural channel network formed by 4,4'-dinitrophenyl

confirms the composite crystal nature of these materials. This knowledge could be utilized in crystal engineering, for example, for designing polar materials for nonlinear optical applications.

Conflicts of interest

There are no conflicts to declare.

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