Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Role of the *gauche* effect and local 1,3-dipole–dipole interactions in stabilizing an unusual conformation of tartarodinitriles

Urszula Rychlewska,* Natalia Waścinska, Beata Warżajtis and Jacek Gawroński

Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland

Correspondence e-mail: urszular@amu.edu.pl

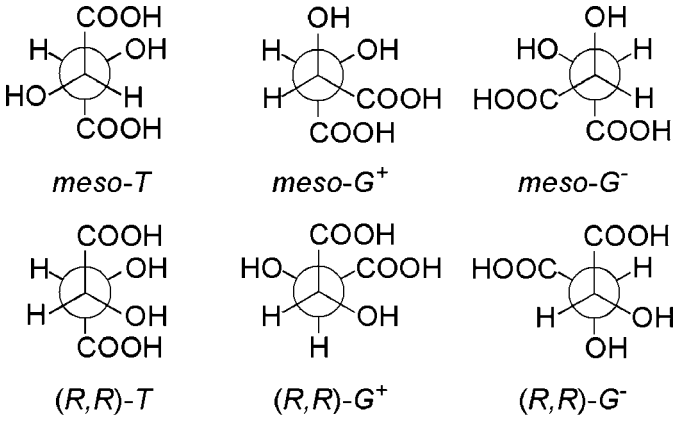
Received 10 March 2008
Accepted 16 June 2008

This paper reports the synthesis, X-ray and NMR investigations of chiral and *meso* dinitriles of tartaric acid (tartarodinitriles) and their *O*,*O*′-diacetyl and *O*,*O*′-dibenzoyl derivatives. While in chiral tartaric acid its esters and NH amides the four-atom carbon chain is overwhelmingly *trans*, it is *gauche* in chiral tartarodinitriles. Conversely, *meso*-tartaric acid, its esters and amides display a tendency for the *gauche* conformation, but *meso*-tartarodinitriles usually have the *trans* conformation. The NMR studies of tartarodinitriles reveal the presence of a conformational equilibrium in solution with a preference for those conformers found in crystals. The *gauche* conformation of *meso*-tartarodinitriles seems to be stabilized by local dipolar interactions, intramolecular C—H···O hydrogen bonds and by a tendency for maximization of the *gauche* effect, the latter effect also operating in chiral tartarodinitriles. Stabilization of the *trans* conformers of tartarodinitriles in the crystals seems to originate from specific intermolecular interactions.

1. Introduction

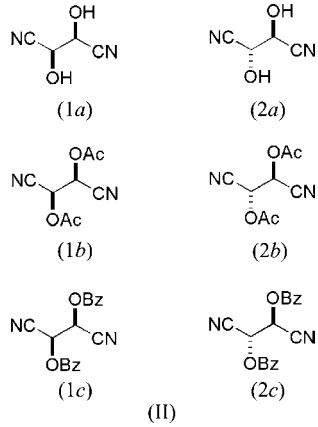
Like tartaric acid, tartarodinitriles can exist in three possible stereoisomeric forms, *i.e.* (*R*,*R*), (*S*,*S*) and *meso* (*R*,*S*) [see (I) overleaf]. One can assume that the lack of optical activity of *meso*-tartaric acid and its derivatives is a result of intramolecular self-compensation owing to the presence in the molecule of either a mirror plane or a centre of symmetry. The first possibility can be ruled out by noting that the eclipsed conformation required is energetically very unfavourable. The other possibility, *i.e.* the utilization of the C_i symmetry, implies, in the case of *meso*-tartaric acid, that all similar groups (*i.e.* OH/OH or COOH/COOH) are in a *trans* (*T*) orientation and hence the molecular dipole moment is equal to zero. The third possibility is that *meso*-tartaric acid adopts the conformation in which similar groups are all in a *gauche* (G^-, G^+) orientation. This is indeed what happens in the crystals of *meso*-tartaric acid and both polymorphic forms of *meso*-tartaric acid monohydrate (Bootsma & Schoone, 1967). All these crystals contain *meso*-tartaric acid molecules in a general position, *i.e.* not displaying any molecular symmetry, with similar groups all in a *gauche* orientation. The lack of molecular symmetry implies that these crystals can be considered as racemic with regard to the conformation of the constituting elements. The same characteristics apply to the crystals of the dimethyl ester of *meso*-tartaric acid (Kroon & Kanters, 1973) and to *meso*-tartaric acid salts such as calcium *meso*-tartrate trihydrate (Vries & Kroon, 1984), and potassium *meso*-tartrate dihydrate (Kroon *et al.*, 1965). With regard to the factors that could stabilize the *gauche* conformation of *meso*-tartrates, a stabilization resulting from the formation of an intramolecular

hydrogen bond has been considered, but the intramolecular hydrogen bonding might not be present in the crystal lattice and thus it can no longer be of primary importance for conformational stability in the solid state.



(I)

As far as the chiral tartaric acid derivatives are concerned, our own studies carried out over two decades (Gawroński *et al.*, 1989, 1997, 2005; Rychlewska & Warżajtis, 2000, 2001; Rychlewska *et al.*, 1997; Rychlewska, 2008) led us to the conclusion that in this group of tartaric acid derivatives the stabilization of the preferred *trans* conformation of the carbon chain is brought about by attractive forces acting between pairs of local C*—H (an asterisk designates a stereogenic center) and CO(carboxylate) dipoles situated (with respect to each other) in a 1,3-position and oriented nearly antiparallel. Moreover, we have recently demonstrated for the case of the dinitrile derivative of (*R*,*R*)-*O*,*O*′-dibenzoyl tartaric acid (Gawroński *et al.*, 2007) that replacement of the carboxylate function by the nitrile group results in a dramatically different conformation, in which the two nitrile substituents are situated in a G^+ orientation and the bulky benzoyl substituents are *trans*. The most obvious explanation was that in the absence of terminal carboxylate functions and the consequent absence of the attractive interactions between CH/CO dipoles the conformation was driven by steric factors, resulting from the presence of the two dibenzoyl substituents. However, in principle, in the absence of terminal carboxylate functions the 1,3 dipole–dipole interactions can still operate within the *gauche* conformation of the carbon main chain, providing that the C*—H dipoles orient nearly parallel to the carbonyl groups of the benzoyl substituents situated at the same chiral atoms. This would create geometrical conditions favoring dipolar interactions between the C*—H and C═O (benzoyl) dipoles in a manner analogous to the interactions between the C*—H bonds and the terminal carboxylate CO groups that are persistently present in numerous chiral tartaric acid derivatives. In spite of that, in neither the crystal structure of the above mentioned (*S*,*S*)-*O*,*O*′-dibenzoyl tartarodinitrile (2*c*) nor in the case of (*S*,*S*)-*O*,*O*′-diacetyl tartarodinitrile (2*b*) reported below did we observe geometries favouring attractive interactions between the C*—H and C═O dipoles. Further insight into the factors that govern the molecular conformation of tartarodinitriles in the solid state could come from the X-ray analysis of the chiral tartarodinitrile possessing unsubstituted hydroxy groups and thus lacking any carbonyl functionality, but so far we have been unable to crystallize this compound. Hence, we have faced two alternatives: either to assume that in the absence of the attractive dipolar interactions the major driving force for molecular conformation of tartarodinitriles is the steric hindrance between the bulky benzoyloxy or acetoxy substituents, or to look for other stabilizing forces. As to the latter option we have considered the well known '*gauche* effect' and a possibility of its multiplication (maximization) in a molecule. To investigate this further we have synthesized a series of *meso* and chiral tartarodinitriles and performed their X-ray and NMR analyses.



(II)

2. Experimental

2.1. Synthesis

meso-2,3-Dihydroxy-2,3-dicyanoethane (1*a*) was isolated from the mixture of (*R*,*R*), (*S*,*S*) and (*R*,*S*)-dinitriles which were obtained in the reaction of glyoxal with potassium cyanide and hydrochloric acid (Pollak, 1894; Grundmann & Fulton, 1964). *meso*-*O*,*O*′-Diacylated derivatives [(1*b*) and (1*c*)] were obtained from tartarodinitrile (1*a*) by acylation with acetic anhydride–pyridine or benzoyl chloride–pyridine.

After a number of trials we were able to obtain and isolate (*S*,*S*)-2,3-dihydroxy-2,3-dicyanoethane (2*a*) in a low yield in the reaction of unprotected (*R*,*R*)-tartaric acid diamide with cyanuric chloride in dimethylformamide–*tert*-butylmethylether (TBME) solution at room temperature (Aquino *et al.*, 2000). The diacetyl (2*b*) and dibenzoyl (2*c*) derivatives of (2*a*) have already been reported (Gawroński *et al.*, 2007). For details see the supplementary data.[1]

2.2. NMR data

The conformations of the dinitrile derivatives of *meso*-tartaric acid [(1*a*), (1*b*) and (1*c*)] and (*R*,*R*)-tartaric acid (2*a*) were studied with the use of ^{1}H NMR and ^{13}C NMR spectra. Both $^3J_{H,H}$ and $^2J_{C,H}$ coupling constants are sensitive to the

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS5062). Services for accessing these data are described at the back of the journal.

Table 1
$^3J_{H,H}$ and $^2J_{C,H}$ coupling constants for dinitriles (1*a*)–(1*c*) and (2*a*)–(2*c*).

Dinitrile	$^3J_{H,H}$ (Hz)†	$^2J_{C,H}$ (Hz)	Solvent
(1*a*)	6.8	−2.5	$(CD_3)_2SO$
(1*b*)	5.5	−4.5	$CDCl_3$
(1*c*)	3.8	−3.9	$(CD_3)_2CO$
(2*a*)	5.1	−4.1	$(CD_3)_2SO$
(2*b*)‡	4.7	−3.5	$CDCl_3$
(2*c*)‡	4.5	−3.8	$(CD_3)_2CO$

† Data from the analysis of side-band splitting. ‡ Data reported by Gawroński *et al.* (2007).

carbon chain conformation, allowing the conformational preferences to be evaluated (Gawroński *et al.*, 1997, 2007). These data are given in Table 1.

2.3. Database mining

A search of the CSD, Version 5.29, November 2007 (Allen, 2002), using *ConQuest* (Bruno *et al.*, 2002) was carried out for all tartaric acid derivatives and salts, excluding metal complexes with the tartrate ions as ligands. The additional search parameters required that structures had three-dimensional coordinates and H-atom positions determined. The search yielded 404 hits which corresponded to 461 independent observations, the majority of them representing chiral tartaric acid derivatives and salts. Only 13 hits (16 observations) related to *meso* tartrates. A CSD search was also carried out to establish the conformational preferences of 1,2-dicyanoethane derivatives. This search has been limited to organic compounds which solely contain tertiary chiral C atoms. This search yielded only five structures.

2.4. X-ray investigations of (1*a*), (1*b*), (1*c*) and (2*b*)

Datasets were collected either at room temperature or at 130 K (for details see Table 2) using a KUMA-CCD diffractometer (Oxford Diffraction, 2007*a*,*b*) equipped with Mo $K\alpha$ radiation. Cell refinement and data reduction were accomplished using *CrysAlisPro* (Oxford Diffraction, 2007*b*). The structures were solved by direct methods using *SHELXS*86 (Sheldrick, 1990) and refined by least-squares refinements on F^2, applying the *SHELXL*97 (Sheldrick, 2008) system of programs. The intensity data were corrected for Lp effects. Anisotropic displacement parameters were employed for the non-H atoms. The positions of the C—H hydrogen atoms were calculated at standardized distances of 0.96 Å except for the O—H H atoms, which were located on difference-Fourier maps. All but the hydroxyl H atoms were refined using a riding

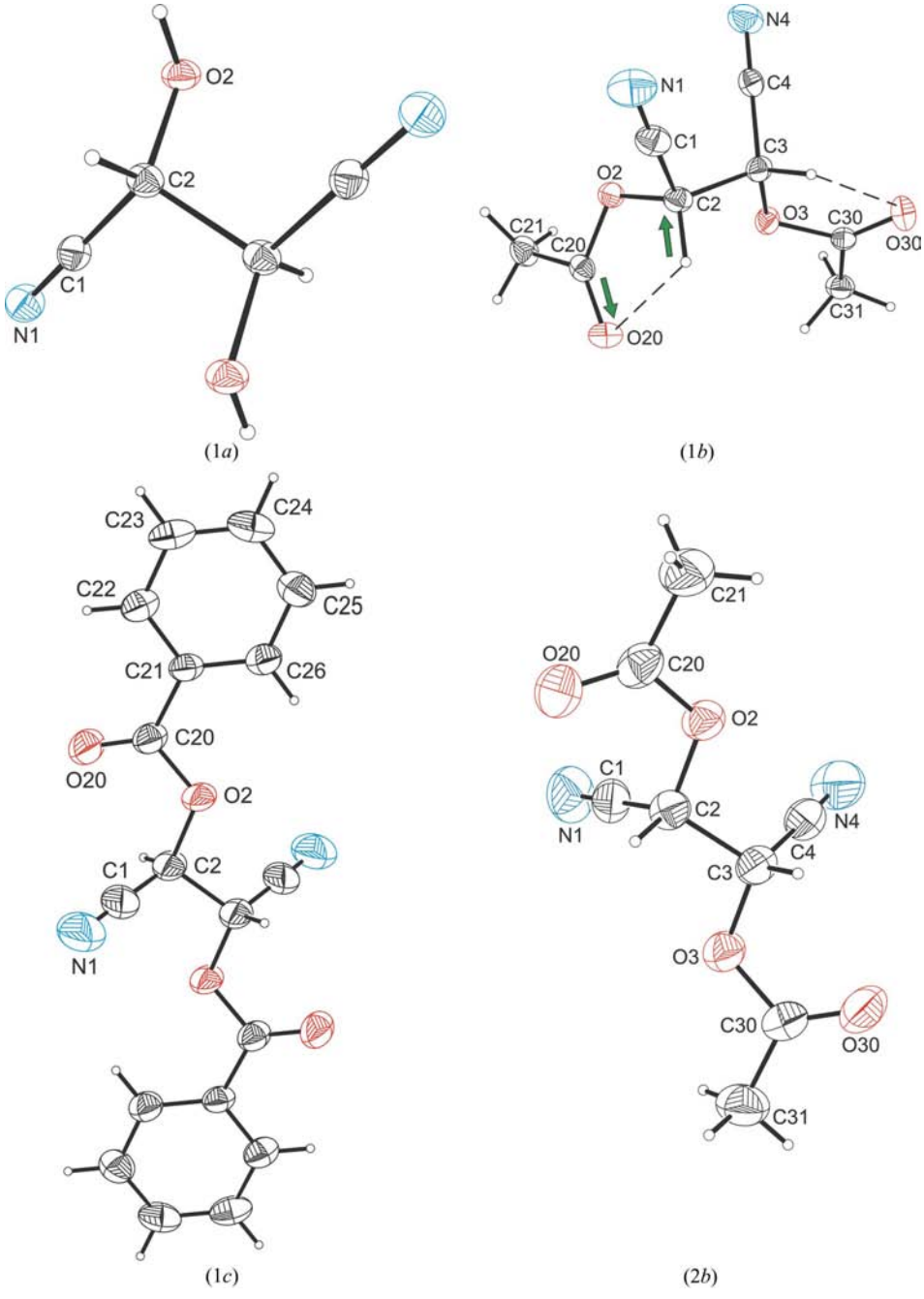


Figure 1
Perspective view of the molecules in the crystals studied. The labelling scheme was used consistently for all the molecules studied. Arrows mark local dipoles and broken lines indicate possible intramolecular hydrogen bonds. Displacement ellipsoids are drawn at the 40% probability level.

Table 2
X-ray experimental details.

	(1*a*)	(1*b*)	(1*c*)	(2*b*)
Crystal data				
Chemical formula	$C_4H_4N_2O_2$	$C_8H_8N_2O_4$	$C_{18}H_{12}N_2O_4$	$C_8H_8N_2O_4$
M_r	112.09	196.16	320.30	196.16
Cell setting, space group	Orthorhombic, *Pbca*	Orthorhombic, *Pbca*	Triclinic, $P\bar{1}$	Orthorhombic, $P2_12_12_1$
Temperature (K)	130 (2)	130 (2)	295 (2)	295 (2)
a, *b*, *c* (Å)	7.2155 (15), 6.2725 (12), 10.828 (2)	12.4510 (4), 8.5089 (3), 18.0764 (5)	5.7840 (14), 7.3241 (18), 10.229 (3)	8.6112 (3), 9.8185 (3), 11.7898 (3)
α, β, γ (°)	90.00, 90.00, 90.00	90.00, 90.00, 90.00	106.26 (2), 105.30 (2), 96.55 (2)	90.00, 90.00, 90.00
V (Å^3)	490.04 (17)	1915.09 (11)	392.90 (18)	996.82 (5)
Z	4	8	1	4
D_x (Mg m^{-3})	1.519	1.361	1.354	1.307
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.13	0.11	0.10	0.11
Crystal form, colour	Prismatic, colourless	Cube, colourless	Plate, colourless	Cube, colourless
Crystal size (mm)	0.50 × 0.35 × 0.20	0.60 × 0.40 × 0.40	0.40 × 0.20 × 0.10	0.55 × 0.50 × 0.40
Data collection				
Diffractometer	Kuma KM4CCD κ geometry	Kuma KM4CCD κ geometry	Kuma KM4CCD κ geometry	Kuma KM4CCD κ geometry
Data collection method	ω scans	ω scans	ω scans	ω scans
Absorption correction	None	None	None	None
No. of measured, independent and observed reflections	2811, 478, 352	7983, 1892, 1438	3310, 1526, 720	7153, 1149, 980
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.039	0.017	0.031	0.013
θ_{max} (°)	26.1	26.1	26.0	26.0
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.118, 1.13	0.029, 0.078, 1.08	0.041, 0.113, 0.87	0.035, 0.099, 1.06
No. of reflections	478	1892	1526	1149
No. of parameters	41	128	109	129
H-atom treatment	Riding	Riding	Riding	Riding
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.1378P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0755P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	< 0.0001	< 0.0001	< 0.0001	< 0.0001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.26	0.15, −0.20	0.14, −0.18	0.19, −0.15
Extinction method	None	*SHELXL*	None	None
Extinction coefficient	–	0.0030 (7)	–	–
Absolute structure	–	–	–	Flack (1983) parameter 0 (10)

Computer programs used: *CrysAlis CCD* (Oxford Diffraction, 2007*a*), *CrysAlis Pro* (Oxford Diffraction, 2007*b*), *SHELXS*86 (Sheldrick, 1990), *SHELXL*97 (Sheldrick, 2008), *XP* (Siemens, 1989), *Mercury* (Bruno *et al.*, 2002).

model and their isotropic displacement parameters were given a value 20% higher than the isotropic equivalent for the atom to which the H atom was bonded. The hydroxyl H atoms were refined isotropically. The *meso*-*O*,*O*′-diacetyltartarodinitrile (1*b*) displays a disorder of the methyl H atoms which adopt two alternative orientations. The occupancy factors refined to 0.70 (1) and 0.30 (1), respectively. The absolute structure of the crystals of (2*b*) was assumed from the known absolute configuration of (*R*,*R*)-tartaric acid which was used as a starting material in the synthesis.

3. Results and discussion

3.1. Results of the CSD search

A search of the CSD, Version 5.29, November 2007 (Allen, 2002), using *ConQuest* (Bruno *et al.*, 2002) on the *meso*-tartaric acid derivatives and salts yielded 16 molecules and ions, of which 12 possessed the all *gauche* and only four the all *trans* conformation, indicating a clear preference of *meso* tartrates for the *gauche* conformation. In only one case was the *trans* conformation imposed by the crystal symmetry (disodium *meso*-tartrate, COZGED; Blankensteyn & Kroon, 1985). The other three ions that adopted the all-*trans* conformation were the constituents of chiral crystals, acting as counterions for chiral amines. Hence their *trans* conformation could not have been forced by the crystal symmetry but, perhaps, resulted from the intermolecular interactions.

The database-mining results presented are in line with several computational studies for 1,2-ethanediol (Csonka *et al.*, 1995; Fornili *et al.*, 2003; Mandado *et al.,* 2004, and references therein), which indicated that the minimum energy corresponds to the *gauche* isomer, in which the two OH groups are optimally oriented for intramolecular hydrogen bonding.

Table 3
Torsion angles (°) describing the molecular conformation.

	(1*a*)	(1*b*)	(1*c*)	(2*b*)
C1—C2—C3(C2*A*)—C4(C1*A*)	180	−57.22 (12)	180	60.24 (21)
O2—C2—C3(C2*A*)—O3(O2*A*)	180	−58.33 (11)	180	179.14 (14)
H2—C2—C3(C2*A*)—H3(H2*A*)	180	−56	180	−57

The all-*trans* conformer has, on average, an energy of 12.56 kJ mol^{-1} above this minimum. However, the presence of intramolecular bonding in the *gauche* conformer of 1,2-ethanediol has been questioned by some of the authors (Mandado *et al.*, 2004). Also the presence of such hydrogen bonding in the solid state might be considered as questionable.

With regards to the 1,2-dicyanoethane derivatives, we have limited our interest to only those containing the tertiary chiral C atoms. Of five such structures deposited in the CSD, four represent *meso* and one a chiral molecule. All the *meso* isomers (CAHVAI, Parfonry *et al.*, 1988; DUPZOD and DUPZUJ, Parfonry *et al.*, 1986; WEJDUK, Koh *et al.*, 1994) adopt the *trans* conformation, required by the space-group symmetry, and the chiral derivative (WEJFAS, Koh *et al.*, 1994) adopts the *gauche* conformation. This finding is fully consistent with the X-ray structure determination results reported below.

3.2. X-ray results

Fig. 1 shows a perspective view of molecules (1*a*), (1*b*), (1*c*) and (2*b*), as found in the crystal lattice.

Torsion angles describing the molecular conformation are listed in Table 3. It follows from this table that in two crystal structures, *i.e.* in dinitriles of *meso*-tartaric acid (1*a*) and *meso*-*O*,*O*′-dibenzoyl tartaric acid (1*c*), we observe the *trans* conformer, with molecules residing on inversion centres, and in one of the crystal structures (1*b*) the molecules in general positions adopt the asymmetric *gauche* conformation. This observation is in contrast to what might have been expected from the CSD search on *meso*-tartrates, where the population of *gauche* conformers is significantly higher than *trans*, but in line with the findings for *meso*-1,2-dicyanoethane derivatives for which only *trans* conformers are present in the CSD (see above). Hence, the *gauche* orientation of the two nitrile groups observed in the crystal structure of (1*b*) is unique for *meso*-1,2-dicyanoethane derivatives. One of the factors that could stabilize this type of conformation is the maximization of the *gauche* effect. The *gauche* conformation of (1*b*) leads to two homo- (CN/CN and OAc/OAc) and one hetero- (CN/OAc) *gauche* effects. In this respect, the C_i symmetrical *trans* conformation seems to be less favourable as it leads to only two pairs of substituents in a mutually *gauche* orientation (OH/CN or OBz/CN, respectively, Fig. 1). The all-*gauche* conformation, observed in (1*b*), also seems favorable from the point of view of the presence of attractive interactions between C*—H/C═O dipoles located 1,3 to each other and oriented antiparallel (Fig. 1). Judging from geometrical parameters, such interactions operate between H2—C2 and C20═O20 dipoles (the angle between the two vectors amounts to 169°) and between H3—C3 and C30═O30 bonds (the angle between the two vectors amounts to 153°). The two types of interactions can also be classified as C—H···O intramolecular hydrogen bonds with H···*A* distances of 2.22 and 2.26 Å, respectively, and *D*—H···*A* angles of 106 and 101°, respectively. One of the C*—H groups is additionally involved in intermolecular hydrogen-bond interactions with the carbonyl oxygen as an acceptor [H3···O20 (at $1-x,\frac{1}{2}+y,\frac{1}{2}-z$) is 2.39 Å and C3—H3···O20 is 139°], but in general there are no strong intermolecular interactions in this crystal structure.

The all-*trans* conformation in the solid state is adopted by *meso*-tartaric acid dinitrile (1*a*) and its *O*,*O*′-dibenzoyl derivative (1*c*). As to the factors that could stabilize this type of conformation, the 1,3-C—H/C═O dipole–dipole interactions are excluded in *meso*-tartaric acid dinitrile, due to the lack of the carbonyl function. They also do not operate in (1*c*), despite the presence of the two carboxylate residues. However, in both crystal structures strong intermolecular interactions are present, *i.e.* in *meso*-tartaric acid dinitrile (1*a*) we notice the formation of intermolecular O—H···N hydrogen bonds [H···N (at $x,\frac{1}{2}-y,\frac{1}{2}+z$) and O—H···N values are 2.01 (3) Å and 162 (2)°, respectively; Fig. 2], while in *meso*-*O*,*O*′-dibenzoyltartarodinitrile (1*c*), the packing is governed by columnar stacks, in which the neighbouring molecules, related by the centre of symmetry, are oriented antiparallel (Fig. 3, Table 4).

With regard to chiral tartarodinitriles, we were not able to obtain crystals of (*R*,*R*)-tartaric acid dinitrile (2*a*), but succeeded in obtaining the crystal structure of the *O*,*O*′-diacetyl- (2*b*) and (previously reported) *O*,*O*′-dibenzoyltartarodinitrile (2*c*). In both cases the molecules adopt a highly unusual conformation in which the carbon chain is bent (G^+) and the bulky acetoxy or benzoyloxy substituents are *trans*. The observed molecular geometry does not favour the dipolar interactions, but the *gauche* effect is multiplied for it relates to three sets of substituents, namely one pair of nitrile groups and

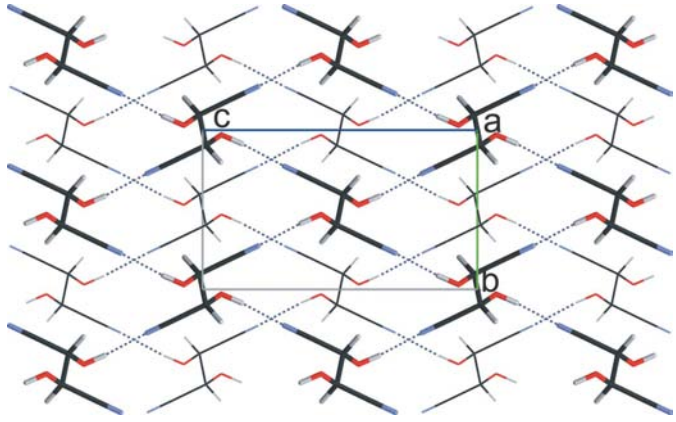


Figure 2
The arrangement of molecules and OH···N hydrogen-bond interactions (broken lines) in the crystal structure of *meso*-tartaric acid dinitrile (1*a*). Thick and thin lines distinguish molecules projected from two different *a*-levels.

Table 4
Parameters describing stacking interactions in the crystals of (1*c*) (Główka *et al.*, 1999).

	Stacking distance *h* (Å)	Offset *r* (Å)	Tilt θ (°)	Twist φ (°)
Ring *A*/Ring *B*	3.510	1.477	0	180
Ring *A*/Ring *C*	3.515	1.488	0	180

Ring *A*: C21—C22—C23—C24—C25—C26; ring *B*: $C21^{i}$—$C22^{i}$—$C23^{i}$—$C24^{i}$—$C25^{i}$—$C26^{i}$; ring *C*: $C21^{ii}$—$C22^{ii}$—$C23^{ii}$—$C24^{ii}$—$C25^{ii}$—$C26^{ii}$. Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $2-x, -y, 1-z$.

two pairs of CN/OBz (or OAc) groups. Since the same number of *gauche* pairs is possible in the *trans* conformer of chiral tartarodinitrile, the exclusively G^{+} conformation adopted by these molecules in the solid state can be accounted for by the supporting role of steric factors which place the bulky benzoyl or acetoxy substituents in a *trans* orientation.

3.3. NMR results

The conformation-averaged coupling constant $^{3}J_{H,H}$, which is larger than 2 Hz for (1*a*)–(1*c*), indicates a contribution of the *T* conformer in which the C2—H and C3—H bonds are antiperiplanar. For (2*a*)–(2*c*) the same is true for a contribution of the G^{-} conformer. The observed average $^{3}J_{H,H}$ coupling constants are in the range 3.5–6.8 Hz, hence they cannot be exclusively due to the *syn* or *anti* arrangement of the C2—H and C3—H bonds in either tartarodinitrile molecule. These data indicate a conformational equilibrium involving *T* and *G* conformers of tartarodinitriles in solution. *meso*-Tartarodinitrile (1*a*) appears to have the highest population of the *T* conformer, as judged by a rather high $^{3}J_{H,H}$ coupling constant (6.8 Hz). This corresponds well to the X-ray diffraction determined structure of (1*a*) and (1*c*) in the crystal in which *meso*-tartarodinitrile molecules display the C_i symmetry.

The coupling constant $^{2}J_{C,H}$ is sensitive to the magnitude of the H—C—C—O*R* torsion angle. *Syn* arrangement results in a negative $^{2}J_{C,H}$ value of the order −6 to −10 Hz, whereas the *anti* arrangement brings about a positive contribution, lowering the magnitude of the $^{2}J_{C,H}$. The dinitriles of both the *meso* and *S*,*S* series are characterized by an intermediate magnitude of $^{2}J_{C,H}$ (Table 1). Thus, in solution both *gauche* and *trans* conformers are apparently in the equilibrium.

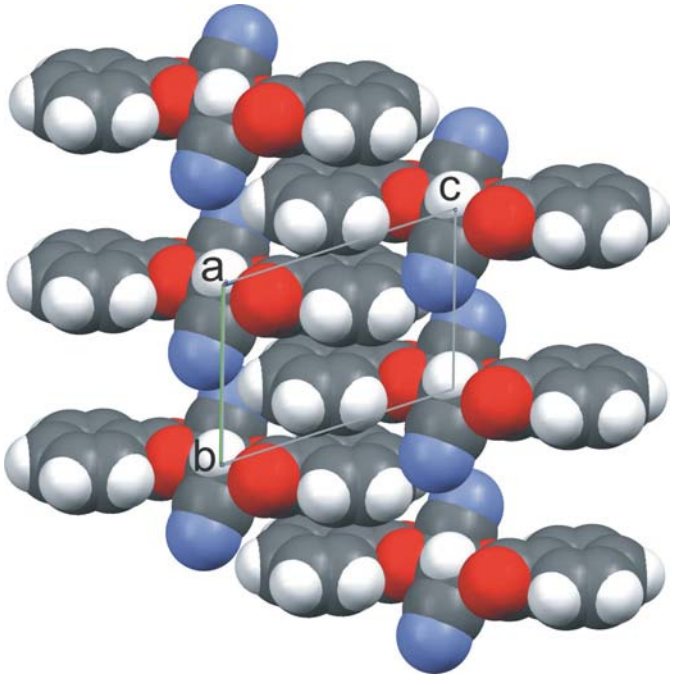


Figure 3
Columnar stacking interactions in the crystal structure of *meso*-*O*,*O*′-dibenzoyltartarodinitrile (1*c*). Atoms are represented by their van der Waals spheres.

4. Conclusions

The outcome for both (*S*,*S*)-tartarodinitriles and *meso*-tartarodinitriles is that they display different conformational preferences than other tartaric acid derivatives and salts. Reported investigations point to the equilibrium of conformers in solution, with a predominance of those that are found in crystals. Our observations seem to indicate that the most common *trans* conformation of *meso*-tartarodinitriles is driven by strong intermolecular interactions in the crystal, while the *gauche* conformation is stabilized by the attractive interactions between C*—H/C═O dipoles located 1,3 to each other. Moreover, a phenomenon consisting of the multiplication of the *gauche* effects, observed in *gauche* conformers of both *meso* and chiral tartarodinitriles, seems to be one of the major structure determining factors.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Aquino, F., Pauling, H., Walther, W., Plattner, D. A. & Bonrath, W. (2000). *Synthesis*, pp. 731–737.
Blankensteyn, A. J. A. R. & Kroon, J. (1985). *Acta Cryst.* C**41**, 182–184.
Bootsma, G. A. & Schoone, J. C. (1967). *Acta Cryst.* **22**, 522–532.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Csonka, G. I., Anh, N., Angyan, J. & Csizmadia, I. G. (1995). *Chem. Phys. Lett.* **245**, 129–135.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fornili, A., Sironi, M. & Raimondi, M. (2003). *J. Mol. Struct. Theochem.* **632**, 157–172.
Gawroński, J., Długokińska, A., Grajewski, J., Plutecka, A. & Rychlewska, U. (2005). *Chirality*, **17**, 388–395.
Gawroński, J., Gawrońska, K. & Rychlewska, U. (1989). *Tetrahedron Lett.* **30**, 6071–6074.
Gawroński, J., Gawrońska, K., Skowronek, P., Rychlewska, U., Warżajtis, B., Rychlewski, J., Hoffman, M. & Szarecka, A. (1997). *Tetrahedron*, **53**, 6113–6144.
Gawroński, J., Gawrońska, K., Waścińska, N., Plutecka, A. & Rychlewska, U. (2007). *Polish J. Chem.* **81**, 1917–1925.
Główka, M. L., Martynowski, D. & Kozłowska, K. (1999). *J. Mol. Struct.* **474**, 81–89.
Grundmann, C. & Fulton, M. B. (1964). *Chem. Ber.* **97**, 566–574.

Koh, L. L., Xu, Y., Sim, K. Y., Liang, E. & Huang, H. H. (1994). *Acta Cryst.* C**50**, 438–442.
Kroon, J. & Kanters, J. A. (1973). *Acta Cryst.* B**29**, 1278–1283.
Kroon, J., Peerdeman, A. F. & Bijvoet, J. M. (1965). *Acta Cryst.* **19**, 293–297.
Mandado, M., Grana, A. M. & Mosquera, A. (2004). *Phys. Chem. Chem. Phys.* **6**, 4391–4396.
Oxford Diffraction (2007*a*). *CrystAlis CCD*. Oxford Diffraction Ltd, Abingdon, England.
Oxford Diffraction (2007*b*). *CrystAlisPro*, Version 1.171. Oxford Diffraction Ltd, Abingdon, England.
Parfonry, A., Declercq, J.-P., Tinant, B., Van Meerssche, M. & Schweiss, P. (1988). *Acta Cryst.* B**44**, 435–440.
Parfonry, A., Tinant, B., Declercq, J.-P. & Van Meerssche, M. (1986). *Acta Cryst.* C**42**, 1266–1267.
Pollak, F. (1894). *Monatsh. Chem.* **15**, 469–488.
Rychlewska, U. (2008). *Engineering of Crystalline Materials Properties: State of Art in Modeling*, edited by J. J. Novoa, D. Braga & L. Addadi, pp. 407–427. Dordrecht: Springer.
Rychlewska, U. & Warżajtis, B. (2000). *Acta Cryst.* B**56**, 833–848.
Rychlewska, U. & Warżajtis, B. (2001). *Acta Cryst.* B**57**, 415–427.
Rychlewska, U., Warżajtis, B., Hoffmann, M. & Rychlewski, J. (1997). *Molecules*, **2**, 106–113.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siemens (1989). *Stereochemical Workstation Operation Manual*, Release 3.4. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
Vries, A. J. de & Kroon, J. (1984). *Acta Cryst.* C**40**, 1542–1544.