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Halogen···halogen contacts for the stabilization of a new polymorph of 9,10-dichloroanthracene

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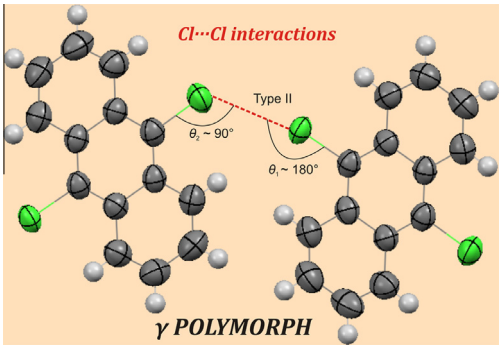
HIGHLIGHTS

- New polymorph of the 9,10-dichloroanthracene is reported.
- Halogen contacts define the packing motif of the crystal structure of the new polymorph.
- DFT-D and MP2 calculations estimates properly the intermolecular interactions present in the system.

GRAPHICAL ABSTRACT



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ABSTRACT

A new polymorph of 9,10-dichloroanthracene (9,10-DCA) namely as γ form, was obtained. The crystal structure of the γ polymorphic system showed an orthorhombic $P2_12_12_1$ space group with $a = 3.8957(2)$ Å, $b = 15.9383(5)$ Å, $c = 17.3107(7)$ Å, $\alpha = \beta = \gamma = 90°$, while the other polymorphs, α and β, crystallized in $P2_1/a$ and P-1 ones, respectively. The intermolecular geometries of γ form were analyzed showing that the crystalline self-assembly of this new polymorph of the 9,10-DCA is stabilized by non-classical C–H···Cl hydrogen bonds, π–π stacking interactions, and mainly by Cl···Cl interactions. Structural parameters confirmed the halogen···halogen contacts correspond to the Type II geometry. Complementary, electronic structure calculations were performed in other to estimate the energetic contribution of the observed intermolecular interactions in the crystal packing of the new system. Density Functional Theory (DFT) considering empirical dispersion corrections (named as DFT-D) and MP2 correlated very well and showed energy values according to previously reported related compounds (e.g., the energy for the Cl···Cl is −5.37 and −3.25 kcal mol^{-1} for MP2/6-31+G** and B2PLYP-D/6-31+G**, respectively). On the other hand, and as expected, DFT using B3LYP as functional was not able to describe properly the studied intermolecular interactions. Moreover, it even predicts repulsive energies for most of the analyzed arrangements.

1. Introduction

Intermolecular interactions, in addition to their structural role, affect the physical and chemical properties of crystalline solids [1,2]. The development of this concept has been one of the priorities of Crystal Engineering, a flourishing interdisciplinary field of

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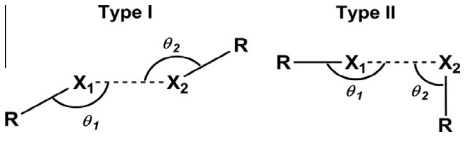
research in modern chemistry with interests in the rational design of functional molecular solids [3]. Although hydrogen bonding and coordination bonds still remain at the forefront of Crystal Engineering strategies, other interactions have received increasing attention over recent years, notably, halogen bonds [4], non-classical hydrogen bonds [5], π–π interactions [6] and halogen···halogen contacts [5d–f]. Intermolecular interactions involving halogen substituents, particularly chlorines, have been observed to enhance crystal formation, providing a tool for Crystal Engineering [7]. These interactions are typically characterized by an inter halogen distance (r_i) that is generally less than the sum of the van der Waals radii ($\sum$vdW; values for $X_1 = X_2$ = Cl, Br and I are 3.5, 3.70 and 3.96 Å respectively [8]). Studies showed that there are two preferred geometries for halogen···halogen interactions (R–$X_1\cdots X_2$–R, X = halogen and R = organic group; Scheme 1). The first arrangement is symmetrical and occurs when $\theta_1 = \theta_2$ (Type I, where θ_1 and θ_2 are the R–$X_1\cdots X_2$ and $X_1\cdots X_2$–R angles, respectively). The second is called Type II and its geometry arises when $\theta_1 = 180°$ and $\theta_2 = 90°$, namely the perpendicular arrangement. Another parameter used to evaluate these contacts is the interaction angle, the dihedral one of the RX_1X_2R moiety (φ) [5,9]. Regarding their nature, there exist some disagreements on the elucidation of whether these close contacts are governed by attractive forces [5d,10] or by minimizing repulsive ones [11]. *Ab initio* calculations in concordance with experimental crystallographic studies showed that in the basis of an electrostatic model, halogen···halogen contacts are directive and a result of attractive forces for all halogens (except fluorine) [12]. A recent study based on experimental charge-density analysis concluded that although Type I geometries are of the van der Waals kind where the dispersion term of the interaction energy prevails on the electrostatic one, the Type II contacts may be understood as attractive $X^{\delta+}\cdots X^{\delta-}$ interactions [7,13].

Other area developed by crystal engineers is the understanding of polymorphism, phenomenon in which a single molecular compound has two or more crystal assembly [14]. Polymorphism is commonly observed among certain chemical species and factors such as, variations in pressure, temperature and polarity of solvents may contribute to changes in the unit cell [15]. Apart from the structural differences, physical properties of each crystal form may differ remarkably thus, controlling the formation of a specific polymorph of desired properties is of special interest in pharmaceutical industries [16]. On the whole, occurrence of polymorphism in organic compounds appears to be very common [15,17]. An example of that, is the 9,10-dichloroanthracene (9,10-DCA). This compounds is well known for its photoluminescence properties and for some applications such as, generation of photoadducts through addition reaction to dienes or initiator for atom transfer radical polymerizations processes [18]. Two crystalline forms of the 9,10-DCA, the α and β polymorph, were discovered through fluorescence and absorption measurements in the 60's [19], but only structural studies of the α form were performed at that time [20a]. Some years later, completed structural studies were reported for the α polymorph [19b] and the single crystal structure of the β one was finally determined [21]. Although the α phase crystallizes from solution at room temperature, the β one can be obtained by heating the α form above 180 °C or directly by sublimation [18–20]. Recently, another crystal form was obtained from a mixture of 9,10-DCA and a very low amount of the dibromo analogue; although its lattice constants are similar to the β polymorph ones, such phase is considered by the authors as a solid solution rather than a new polymorph [22]. In the present work, a new polymorphic structure of the 9,10-DCA, named γ form, is reported. The supramolecular analysis revealed the presence of Cl···Cl contacts in this new solid form, which were not present in the previously reported structures. Due to its nature, such interactions play a key role in the packing and stability of this new form.



Scheme 1. Geometries for halogen···halogen contacts. Type I, where $\theta_1 = \theta_2$; and Type II with $\theta_1 = 180°$ and $\theta_2 = 90°$ (R = organic group, X = Cl, Br and I).

In addition to the experimental data, second-order Møller–Plesset (MP2) theoretical calculation method was employed for the evaluation of the interplay of the intermolecular interactions present in the supramolecular motifs. This high-level *ab initio* method is known to be capable of properly describing weak intermolecular interactions such as, non-classical hydrogen bonds and π–π interactions [23]. Furthermore, taking as reference the MP2 results, Density Functional Theory (DFT) calculations augmented with empirical dispersion correction (DFT-D) were also performed in order to correlate these two methodologies. DFT-D methods, which consists of adding a pairwise interatomic C_6R^{-6} term to the DFT energy, have proven to be accurate for a large range of chemical systems where non-covalent forces play an important role [24] and even for the prediction of polymorphism [25]. Nevertheless, according to our knowledge, there are just a few examples in literature where DFT calculations with van der Waals corrections are used to describe intermolecular interactions involving halogen atom [26]. Thus, in addition to reporting the new polymorph of the 9,10-DCA, we chose the DFT-D computational methodology to support the theoretical foundations regarding its supramolecular behavior.

2. Experimental

2.1. Crystallization procedure

9,10-Dichloroanthracene 98% purchased from Sigma–Aldrich, was dissolved and purified by a chromatography column on silica gel to remove impurities using cyclohexane as solvent. The solvent was then removed with a rotary evaporator. Yellow crystals of the γ polymorph of 9,10-dichloroanthracene, suitable for X-ray structure determination, were obtained after dissolving the solid in a small amount of an 1:1 acetonitrile/methylenechloride mixture and letting the solution on the refrigerator for several days.

2.2. X-ray diffraction experiments

Room temperature X-ray diffraction data collection (φ scans and ω scans with κ offsets) was performed on an Enraf-Nonius Kappa-CCD diffractometer (95 mm CCD camera on κ-goniostat) using graphite-monochromated MoKα radiation (0.71073 Å). Data were collected up to 50° in 2θ, with a redundancy of 4. The final unit cell parameters were based on all reflections. Data collections were made using the COLLECT program [27]; integration and scaling of the reflections were performed with the HKL Denzo–Scalepack system of programs [28]. Multi-scan absorption correction was applied [29].

The structure was solved by direct methods with SHELXS-97 [30]. The model was refined by full-matrix least squares on F^2 with SHELXL-97 [30]. All the hydrogen atoms were stereochemically positioned and refined with the riding model [30]. Aromatic hydrogen atoms were set isotropic with a thermal parameter 20% greater than the equivalent isotropic displacement parameter of the atom to which each one was bonded. The programs SHELXL-97 [30], and ORTEP-3 [31] and Mercury [32] were used within WinGX [33] to prepare materials for publication. Data collections and experimental details for γ-9,10-DCA are summarized in Table 1.

2.3. Computational details

The evaluation of the intermolecular interactions in the new polymorphic system was done in three steps. First of all, the B3LYP functional, a commonly used strategy for the chemist community [34], was employed for getting a suitable account of these interactions. However, due to the lack of long-range correlation, the conventional Density Functional Theory (DFT or HF) methods are usually insufficient to describe the noncovalent interactions [35]. In order to get a more appropriate description of the weak interactions energies the second-order Møller–Plesset (MP2) approach, which includes a large portion of the correlation effects, was applied [23]. Finally, a Density Functional Theory method with semi-empirical dispersion correction using the functional B2PLYP-D [36], known as DFT-D [23], was employed to test its performance in describing the intermolecular interactions exhibited in this system. The intermolecular interaction energies were computed according Eq. (1). The energy of the monomer and the corresponding dimer were obtained from single point energy calculations obtained using the crystallographic molecular conformations. For a trimer, an analogous equation was used but considering three molecules of the monomer. Atomic charges were calculated using NPA schemes [37]. All calculations were performed with the ORCA program (version 2.9) [38] using the 6-31G and 6-31+G** basis sets [39]. This program presents different basis sets options that allow the user to evaluate the weight of the studied parameters in the theoretical analysis of the intermolecular interactions. However, the 6-31+G** basis set is considered to be the most appropriate one for these kinds of interactions.

$$E_{int} = E_{dim} - 2.E_{mon} \quad (1)$$

3. Results and discussion

3.1. Molecular and supramolecular structure

The new polymorph of 9,10-DCA reported in this work, named as γ form, crystallized in an orthorhombic non-centrosymmetric space group $P2_12_12_1$. On the other hand, the α and β forms crystallized as centrosymmetric space group $P2_1/a$ and P-1, respectively [19–21]. For the comparative analysis the structures DCLANT10 corresponding to the α polymorphs and DCLANT01 to the β one, will be used [19b,20a]. Fig. 1 shows an ORTEP type view of the asymmetric unit of γ-9,10-DCA showing the corresponding rings and the non-hydrogenous atoms labels. The molecular conformation observed for this modification is similar to the one presented by the α- and β-9,10-DCA forms.

Using the Mogul program [40], a knowledge base of molecular geometry derived from the Cambridge Structural Database (CSD) [41], the intramolecular parameters of the reported structure were compared with corresponding ones from similar molecules deposited at the CSD and thus, it was found that all bond lengths and angle agree with the expected values. The main geometrical parameters are given in Table 2.

Concerning the conformation of the rings (Fig. 1), the structural analysis shows that the anthracene system is planar with a r.m.s of 0.0083, being the biggest deviation from the least-squares plane of 0.021(5) Å for C7, without including the chlorine substitutions. When the two halogen atoms are considered, C7 also presents the largest deviation (0.022(5) Å) and a r.m.s deviation for the sixteen fitted atoms of 0.0106. Furthermore, if comparing each ring individually, they are also practically planar, being the largest deviations from the individual least-squares planes 0.006(3) Å for C1 (r.m.s deviation of the fitted atoms = 0.0037), 0.013(4) Å for C6 (r.m.s deviation of the fitted atoms = 0.0076) and 0.005(3) Å for C5A (r.m.s deviation of fitted atoms = 0.0036), respectively.

The molecular analysis of the three polymorphs of 9,10-DCA indicates that their conformations are similar but as a consequence of different weak intermolecular interactions, each system presents a distinctive crystal packing (Fig. 2). As for the γ polymorph, the α and β forms show C–H···Cl non-classical H-bonds with H···Cl distances of 2.95–3.05 Å and 2.99–3.03 Å, respectively. In the previously reported polymorphs these contacts give place to corrugated like planes along the crystallographic planes *bc* and *ab* for the α and β forms, respectively (Fig. S1, ESI). On the other hand, in the three crystal phases π–π intermolecular interactions are clearly observed. The three polymorphs exhibit an *offset* face to face arrangement. In polymorph α with a 1.1° angle between the planes described by the aromatic rings and a distance between centroids of 3.752–3.834 Å, and in a perfectly parallel geometry for the β and γ forms with distance between centroids of 3.700–3.869 Å and 3.792–3.784 Å, respectively (Fig. S2, ESI). Owing to the presence of such interactions, columns along the crystallographic axes are observed for the α and β forms. Those

Table 1
Crystal data collection and structure refinement parameters for γ-9,10-DCA.

Parameters	γ-9,10-DCA
Molecular formula	$C_{14}H_8Cl_2$
Empirical formula	$C_7H_4Cl_1$
Formula weight	247.10
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions (Å)	a = 3.8957(2)
	b = 15.9383(5)
	c = 17.3107(7)
Volume (Å^3)	1074.84(8)
Z	4
Calc. density (Mg/m^3)	1.527
Absorp. coefficient (mm^{-1})	0.566
$F(000)$	504
Crystal size (mm^3)	0.04 × 0.09 × 0.31
θ Range for data collection	3.76–26.00
Index ranges	$-3 \leqslant h \leqslant 4$, $-19 \leqslant k \leqslant 19$, $-19 \leqslant l \leqslant 21$
Reflections collected	13,123
Independent reflections	2082 [R(int) = 0.0991]
Completeness to $\theta_{Max.}$ (%)	98.8
Data/restraints/parameters	2082/0/146
Goodness-of-fit on F^2	1.054
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0586, $wR2$ = 0.1653
R indices (all data)	$R1$ = 0.0713, $wR2$ = 0.1778
Largest diff. peak and hole	0.576 and −0.282 e Å^{-3}

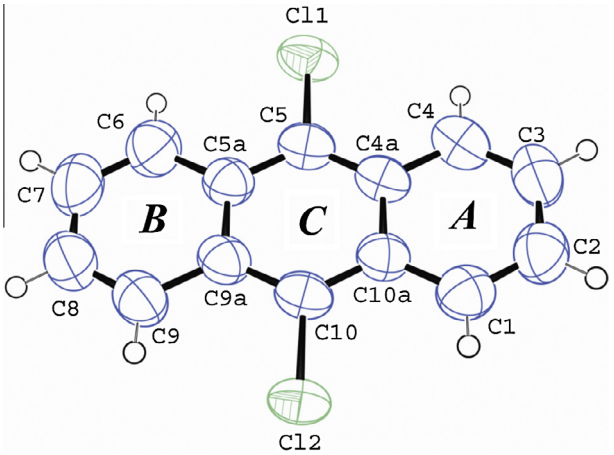


Fig. 1. Asymmetric unit of γ-9,10-DCA, showing atom-numbering scheme. Displacement parameters ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Table 2
Bond lengths (Å) and angles (°) for γ-9,10-DCA.

Cl(2)–C(10)	1.798(4)	C(10A)–C(10)–C(9A)	123.3(4)
Cl(1)–C(5)	1.766(4)	C(10A)–C(10)–Cl(2)	119.3(3)
C(6)–C(7)	1.361(7)	C(9A)–C(10)–Cl(2)	117.3(3)
C(6)–C(5A)	1.414(6)	C(2)–C(1)–C(10A)	121.4(4)
C(5)–C(4A)	1.390(6)	C(1)–C(2)–C(3)	120.4(4)
C(5)–C(5A)	1.404(6)	C(3)–C(4)–C(4A)	122.0(4)
C(8)–C(9)	1.332(7)	C(10)–C(9A)–C(9)	123.9(4)
C(8)–C(7)	1.418(7)	C(10)–C(9A)–C(5A)	118.1(4)
C(10A)–C(10)	1.392(6)	C(9)–C(9A)–C(5A)	118.0(4)
C(10A)–C(1)	1.414(6)	C(5)–C(5A)–C(6)	122.9(4)
C(10A)–C(4A)	1.440(6)	C(5)–C(5A)–C(9A)	118.3(4)
C(10)–C(9A)	1.402(6)	C(6)–C(5A)–C(9A)	118.8(4)
C(1)–C(2)	1.371(7)	C(5)–C(4A)–C(4)	123.2(4)
C(2)–C(3)	1.415(7)	C(5)–C(4A)–C(10A)	118.6(4)
C(4)–C(3)	1.357(7)	C(4)–C(4A)–C(10A)	118.2(4)
C(4)–C(4A)	1.422(6)	C(6)–C(7)–C(8)	120.5(5)
C(9A)–C(9)	1.434(6)	C(4)–C(3)–C(2)	119.7(5)
C(9A)–C(5A)	1.442(5)	C(8)–C(9)–C(9A)	121.1(4)
C(7)–C(6)–C(5A)	120.6(5)		
C(4A)–C(5)–C(5A)	123.2(4)		
C(4A)–C(5)–Cl(1)	119.0(3)		
C(5A)–C(5)–Cl(1)	117.8(4)		
C(9)–C(8)–C(7)	121.0(5)		
C(10)–C(10A)–C(1)	123.3(4)		
C(10)–C(10A)–C(4A)	118.5(4)		
C(1)–C(10A)–C(4A)	118.2(4)		

arrangements are then interacting through the abovementioned C–H···Cl contacts and therefore, a 3D supramolecular network is exhibited. A more detailed analysis of the intermolecular interactions and supramolecular behavior of the γ-9,10-DCA is presented in the next paragraphs.

As discussed, C–H···Cl contacts and π–π stacking interactions are observed for the three polymorphs of the 9,10-DCA but, only the new γ form shows Cl···Cl contacts (Fig. 3). The halogen···halogen interactions give rise to infinite chains along the crystallographic *b* axis (Fig. 3a), in which the molecules are related by a 2-fold screw axis. The intermolecular separation Cl1···Cl2 is 3.557(2) Å, value barely larger than twice the spherical chlorine van der Waals radius (3.52 Å) and in agreement with several reported structures where these kinds of interactions were considered [13]. The C5–Cl1···Cl2 and C10–Cl2···Cl1 angles are 112.43° and 158.35°, respectively, with a φ dihedral angle of 73.82°. Based on the mentioned features, the interaction can be described as Type II geometry (Fig. 3b and Scheme 1). An statistical analysis of the CSD database for Cl···Cl interactions shows that the Type II is the most common geometry found in halogens–halogens interactions, with the exception of fluorine [11]. This analysis also shows that the relative strengths of the halogen···halogen contacts depend on the hybridization of the *ipso* carbon decreasing in the following order: $sp^2 > sp > sp^3$ [11]. The C–Cl bond lengths in the three forms are different. This differences are related with the presence or absence of intermolecular interaction involving the Cl atom [5,42]. In the α and β forms the C–Cl bond length range is 1.734–1.746 Å because no halogen-halogen interactions are observed. However, in the γ form, the C–Cl bond length range is larger (1.765 and 1.790 Å) due to the presence of this interaction. All these structural features confirm not only the existence of the halogen–halogen intermolecular contact on the new polymorph but also its relevance on the compound stability and crystal packing.

The analysis of the crystal packing of the γ form also shows the presence of C–H···Cl non-classical hydrogen. Fig. 4a shows that the C6–H6···Cl1 interaction form a 1D helicoidal infinite arrangement along the *a* axis. The 3D network is completed by the above mentioned Cl···Cl contacts which connect the chains stabilizing the molecules along the *bc* plane (Fig. 4b and c). In the C6–H6···Cl1 interaction the H···C separation is 2.894(1) Å, the CHCl angle is 132.9(3)° and a donor-acceptor (C6···Cl1) distance is 3.592(5) Å.

The crystal packing is also stabilized by π–π stacking interactions, due to an *offset* face-to-face (*off*) orientation of the anthracene rings [3] (Fig. 5). This supramolecular organization was also found in others three-fused rings related compounds [43]. In this interaction the molecules are related by translational symmetry along the crystallographic *a* axis and the anthracene rings are parallel with the corresponding centroids accordingly displaced. The centroids Cg1, Cg2 and Cg3, in the *A*, *B* and *C* rings respectively, show offset angles and separation distances of 3.792(3) Å and 22.35°, and 3.784(3) Å and 22.09° for the Cg1–Cg3 and Cg2–Cg3 interactions, respectively (see Figs. 1 and 5).

3.2. Theoretical evaluation

The main intermolecular interactions present in the new polymorph were investigated by electronic structure calculations using MP2, DFT and DFT-D. For the analysis, two dimers (D1 and D2) and a trimer (T) were defined using the crystallographic conformations. Dimer 1 (D1) is described by the halogen···halogen interaction (Fig. 3 and S3, ESI), dimer 2 (D2) by the non-classical hydrogen bond (Fig. 4a and S3, ESI) and the trimer (T) is the moiety defined above at the crystallographic *bc* plane (Fig. 4b and c and S3, ESI), where both kinds of contact are observed. Table 3 summarizes the obtained values for the stabilization energy of each entity.

DFT-D computed values are in agreement with the results obtained with the MP2 approach, a well-established method for the evaluation of non-covalent interactions (variability between methods is among 0.5 and 5.1 kcal mol^{-1} depending on the basis set used in the calculation, Table 3). Even with the smaller basis set, the values are reliable (Table 3). These results support the hypothesis that the crystal packing is stabilized by halogen···halogen interactions and non-classical H-bonds. We estimate that these two schemes prevail over the stacking interactions among aromatic rings which were not taken into account for the energetic analysis. Based on the structural parameters and calculated results, the observed H-bond may be classified as weak [44]. The values obtained for the halogen contacts on γ-9,10-DCA are in agreement with the reported ones for the Cl···Cl contact in the model of two

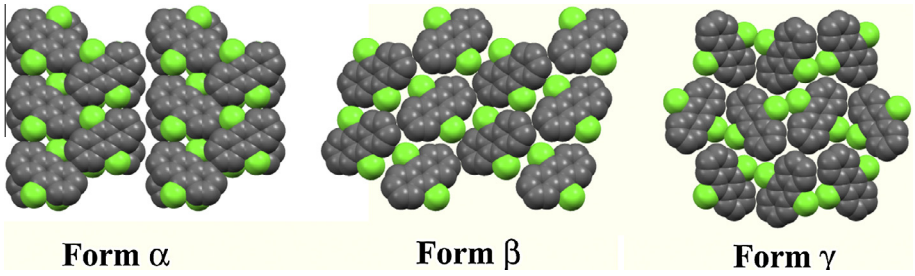


Fig. 2. Spacefill representation showing the differences in the crystal packing of three polymorphs. For clarity reasons hydrogen atoms are not shown. For the α and β polymorphs, structures DCLANT10 and DCLANT01 respectively, were used.

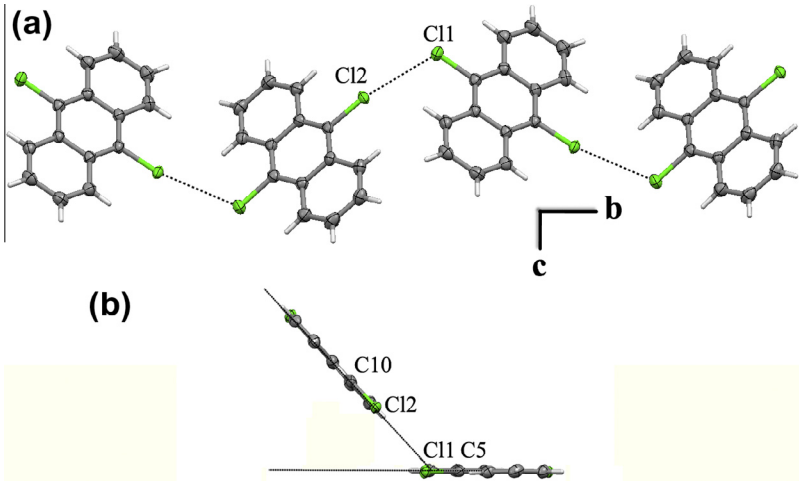


Fig. 3. (a) Cl···Cl interactions between molecules of 9,10-DCA related by two-fold screw axis. (b) Directionality of the Cl···Cl interaction in the γ form.

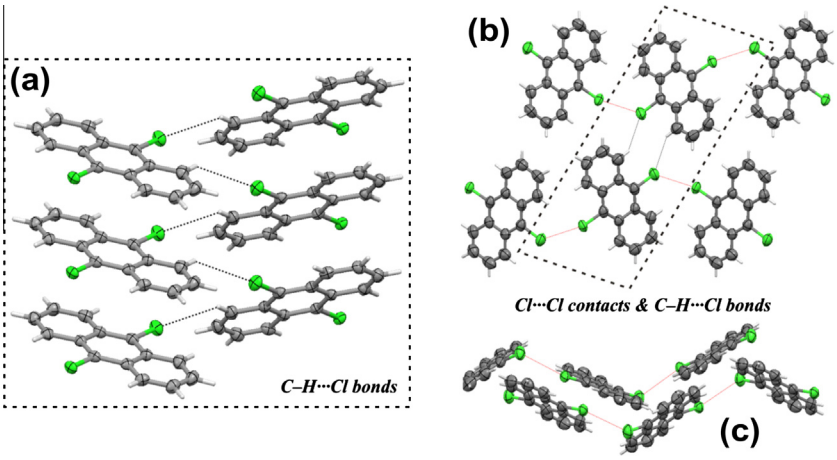


Fig. 4. Non-classical C–H···Cl hydrogen bonds (black dashed lines) observed in γ-9,10-DCA giving place to an infinite helicoidal chain (a) and a corrugated *bc* plane through the C–H···Cl hydrogen bonds and Cl···Cl contacts (b and c) view along the *a* axis.

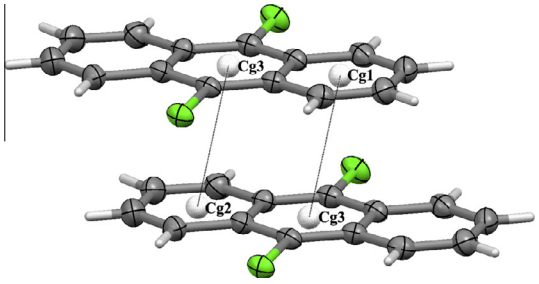


Fig. 5. π–π Stacking interactions of γ-9,10-DCA showing the geometry between the centroids.

Table 3
Computed energy in kcal mol^{-1} for the intermolecular interactions present in γ-9,10-DCA.

	DFT/B3LYP		DFT-D/B2LYP-D		MP2	
	6-31G	6-31+G**	6-31G	6-31+G**	6-31G	6-31+G**
D1 [Cl···Cl]	0.24	0.59	−2.42	−3.25	−2.19	−5.37
D2 [C–H···Cl]	−0.18	0.22	−2.03	−2.47	−1.80	−3.95
T [Cl···Cl···H–C]	−0.22	0.74	−5.90	−7.59	−5.37	−12.62

interacting chlorobenzene molecules (ref. [11], *E*: −1.315 kcal mol^{-1} MP2/triple-zeta basis set for C and H atoms and with diffuse functions for the halogen). Although there is a small difference between the energies of each kind of contacts (0.4–1.4 kcal mol^{-1}, Table 3), Cl···Cl interactions seem to be stronger than the Cl···H–C ones, reinforcing the idea of the role of the halogen···halogen synthons in supramolecular chemistry. The energy values for the trimer are similar to the sum of the energy of each independent dimer but, as expected, with stabilization energies between 1.4 kcal and 3.3 mol^{-1} depending on the method and basis set (Table 3) used. On the other hand, DFT/B3LYP calculations showed to be strongly dependent on the basis set. It is important to mention that, in most of the cases, this method wrongly predicts a repulsive nature of the investigated interactions. Consequently, we assume that this method is not reliable to describe the non-covalent interactions in this system and, probably, in related ones as well.

As pointed out, geometrically, the halogen···halogen contact could be described as a Type II kind (Scheme 1). The different environment around each chlorine atom due to the presence of the H-bond between Cl1 and H6 (Fig. 4b) stresses the suggested oppositely polarized regions which give place to an electrophilic–nucleophilic interaction. This is in agreement with the attractive model for the halogen–halogen contact discussed above. A qualitative evidence to analyze this, can be addressed through the

calculation of the atomic charges of the involved atoms. Using the NPA schemes it was observed that the calculated charge of each chloride atom is different in both, the trimer and the dimer D1 (Table S1, ESI), supporting the proposed analysis.

4. Concluding remarks

Changes in the crystallization procedure gave place to a new crystal form of 9,10-dichloroanthracene, the γ polymorph. Its supramolecular habit showed substantial changes respect to the other two known polymorphs, being the halogen···halogen contact the most relevant difference. Based on the reported models and the structural parameters such a contact can be described as a Type II kind, where the nature of the interaction is understood as electrostatic. In addition, theoretical calculations were performed in order to comprehend and evaluate the role of the intermolecular interaction present in the crystal packing of the new polymorph. DFT methods including semi empirical corrections and MP2 approaches agreed well, and showed energy values for the Cl···Cl synthon in agreement with the reported ones for related systems. On the other hand, DFT/B3LYP resulted to be inappropriate to describe the analyzed contacts. Finally, once more, the new compound reported here accounts the importance of the halogen-halogen contacts in the stability of the crystal packing and exemplify also, the relevancy of these kinds of intermolecular interactions as tool for Crystal Engineering.

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Appendix A. Supplementary material

Electronic Supplementary Information (ESI) associated with this article can be found, in the online version. Supplementary crystallographic data sets for γ-9,10-DCA are available through the Cambridge Structural Data Base, deposition number CCDC 946000. Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 123 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.ac.uk). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.11.028.

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