Molecular and crystal structure of 2-cyano-(2*E*)-pentadien-2,4-oic acid and ethyl-2-cyano-(2*E*)-pentadien-2,4-oate*

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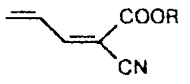
X-ray study of 2-cyano-(2*E*)-pentadien-2,4-oic acid (**1**) and its ethyl ester (**2**) showed that the molecules of **1** and **2** in the crystalline phase form stacks by translating along the shortest crystallographic axis. The nature of the intermolecular interactions favoring the formation of such β-structures was analyzed within the framework of the Bader topological theory. Possible routes of topochemical reactions of compounds **1** and **2** are considered.

Key words: 2-cyano-(2*E*)-pentadien-2,4-oic acid, ethyl-2-cyano-(2*E*)-pentadieno-2,4-oate, molecular structure, crystal structure, C—H...O bond, *ab initio* calculations, β-structure, topochemical reactions.

In continuation of a systematic study of the structure and reactivity of 2-cyanoacrylates,[1] we performed an X-ray study of their vinyl analogs, 2-cyano-(2*E*)-pentadien-2,4-oic acid (**1**) and its ethyl ester (**2**). The interest in these compounds is explained by their ability to undergo anionic polymerization and copolymerization under mild conditions.[2] In addition, topochemical reactions can occur in 2-cyanopentadien-2,4-oates, as in other electron-deficient butadiene derivatives.[3]



1: R = H
2: R = Et

Experimental

Compounds **1** [4] and **2** [5] were synthesized using the known procedures. Crystals suitable for X-ray study were obtained by isothermic evaporation of an ether solution of **1** and a hexane solution of **2**. The ^{13}C NMR spectrum of compound **1** was recorded on a Bruker AMX-400 spectrometer (100.68 MHz) in deuterated acetone (δ): 162.03 C(1), 113.72 C(2), 132.02 C(3), 154.40 C(4), 134.34 C(5), 107.01 C(6).

X-ray study. Crystals of compound **1** ($C_6H_5O_2N$) are monoclinic. At −80° C, a = 3.779(2) Å, b = 11.747(7) Å, c = 13.708(7) Å, β = 90.10(5)°, V = 608.5(6) Å^3, space group $P2_1/c$, Z = 4, d_{calc} = 1.344 g cm^{-3}, and μ = 0.103 mm^{-1}. The intensities of 2708 reflections (1211 independent reflections, R_{int} = 0.104) were measured on a four-circle automatic Syntex P2$_1$/PC diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scan, 2θ$_{max}$ = 54°). The structure was solved by direct methods using the SHELXTL PLUS 5 program package.[6] Positions of H atoms were calculated geometrically and refined using the riding model with fixed U_{iso} values (U_{iso} = 1.2U_{eq}) of the non-hydrogen atoms bonded to the given H atoms. The full-matrix LSM F^2-refinement in anisotropic approximation for non-hydrogen atoms (82 parameters, 860 reflections) was conducted to R_1 = 0.082 (for 531 reflections with $F > 4\sigma(F)$), wR_2 = 0.18, and S = 1.18. The atomic coordinates for compound **1** are listed in Table 1, and the bond lengths and bond angles are given in Tables 2 and 3, respectively.

Crystals of compound **2** ($C_8H_9O_2N$) are monoclinic. At 20 °C, a = 4.256(3) Å, b = 15.83(1) Å, c = 12.370(5) Å, β = 94.22(4)°, V = 831.2(9) Å^3, space group $P2_1/c$, Z = 4, d_{calc} = 1.208 g cm^{-3}, and μ = 0.088 mm^{-1}. The intensities of 1671 reflections (1464 independent reflections, R_{int} = 0.097) were measured on a four-circle automatic Siemens P3/PC diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scan, 2θ$_{max}$ = 50°). The structure was solved by direct methods using the SHELXTL PLUS 5 program package.[6] The

Table 1. Coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2×10^3) of non-hydrogen atoms in structure **1**

Atom	x	y	z	U_{eq}
N(1)	4390(13)	6296(3)	3176(3)	54(1)
O(1)	5221(9)	8687(2)	4596(2)	47(1)
O(2)	2393(10)	10150(2)	3909(2)	48(1)
C(1)	3458(11)	9106(3)	3936(3)	35(1)
C(2)	2525(11)	8401(3)	3073(3)	35(1)
C(3)	944(12)	8834(3)	2279(3)	40(1)
C(4)	42(12)	8208(3)	1407(3)	38(1)
C(5)	−1561(14)	8713(4)	659(3)	50(1)
C(6)	3526(12)	7221(3)	3128(3)	39(1)

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* Dedicated to the memory of Academician M. I. Kabachnik on his 90th birthday.

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Table 2. Bond lengths (*d*) in structures **1** and **2**

Bond	*d*/Å	Bond	*d*/Å
Structure **1**		Structure **2**	
N(1)—C(6)	1.136(5)	O(1)—C(1)	1.198(3)
O(1)—C(1)	1.226(5)	O(2)—C(1)	1.339(3)
O(2)—C(1)	1.291(5)	O(2)—C(7)	1.464(3)
C(1)—C(2)	1.486(5)	N(1)—C(6)	1.143(3)
C(2)—C(3)	1.340(6)	C(1)—C(2)	1.498(3)
C(2)—C(6)	1.440(5)	C(2)—C(3)	1.348(4)
C(3)—C(4)	1.444(6)	C(2)—C(6)	1.432(4)
C(4)—C(5)	1.329(6)	C(3)—C(4)	1.439(4)
		C(4)—C(5)	1.337(4)
		C(7)—C(8)	1.505(4)

Table 3. Bond angles (ω) in structures **1** and **2**

Angle	ω/deg	Angle	ω/deg
Structure **1**		Structure **2**	
O(1)—C(1)—O(2)	124.9(4)	C(1)—O(2)—C(7)	114.2(2)
O(1)—C(1)—C(2)	119.4(4)	C(3)—C(4)—C(5)	122.1(3)
O(2)—C(1)—C(2)	115.6(4)	C(2)—C(3)—C(4)	125.8(3)
C(3)—C(2)—C(6)	121.6(4)	C(3)—C(2)—C(6)	121.2(2)
C(1)—C(2)—C(3)	122.7(4)	C(1)—C(2)—C(3)	119.6(2)
C(1)—C(2)—C(6)	115.7(3)	C(1)—C(2)—C(6)	119.2(2)
C(2)—C(3)—C(4)	125.7(4)	O(1)—C(1)—O(2)	124.5(2)
C(3)—C(4)—C(5)	121.2(4)	O(1)—C(1)—C(2)	123.3(2)
N(1)—C(6)—C(2)	178.5(5)	O(2)—C(1)—C(2)	112.3(2)
		O(2)—C(7)—C(8)	108.0(2)
		N(1)—C(6)—C(2)	177.2(3)

positions of hydrogen atoms were found from a difference synthesis. The full-matrix LSM F^2-refinement (136 parameters, 1434 reflections) in anisotropic (isotropic for hydrogen atoms) approximation was conducted to $R_1 = 0.079$ (for 1036 reflections with $F > 4\sigma(F)$), $wR_2 = 0.209$, and $S = 1.03$. The atomic coordinates for compound **2** are listed in Table 4, and the bond lengths and bond angles are given in Tables 2 and 3, respectively.

Ab initio quantum-chemical calculations of the wave functions for the dimers of compounds **1** (**1**—**1**′ ($1 - x$, $2 - y$, $1 - z$), **1**—**1**″ ($x - 1$, $1.5 - y$, $-0.5 + z$), **1**—**1**‴ ($1 + x$, y, z)) and **2** (**2**—**2**′($-x$, $1 - y$, $2 - z$)) were performed at the HF/6-31G** level of theory with fixed geometry taken from the data of X-ray study using the GAMESS program.[7] The topological analysis of the electron density (ED) function was carried out using the EXTREME program incorporated into the AIMPAC software package.[8]

Results and Discussion

The 2-cyanopentadienoate fragments of molecules **1** and **2** (Fig. 1, 2) are flattened despite the shortened intramolecular H(4)...C(6) contacts (2.66 Å, the sum of the van der Waals radii is 2.87 Å).[9] The maximum deviations from the planes passing through all non-hydrogen atoms of these fragments are 0.07 and 0.03 Å in the molecules of **1** and **2**, respectively. The bond lengths in the 2-cyano-pentadiene fragments of mol-

Table 4. Coordinates of non-hydrogen atoms (×10⁴, for hydrogen atoms ×10³) and equivalent isotropic thermal parameters (Å²×10³) in structure **2**

Atom	*x*	*y*	*z*	U_{eq}
N(1)	7400(6)	3252(1)	7301(2)	42(1)
O(1)	534(5)	3797(1)	10052(2)	43(1)
O(2)	2969(4)	2666(1)	9403(1)	33(1)
C(1)	2242(6)	3489(2)	9433(2)	31(1)
C(2)	3832(6)	3990(2)	8604(2)	31(1)
C(3)	3311(6)	4828(2)	8520(2)	34(1)
C(4)	4564(7)	5382(2)	7737(2)	38(1)
C(5)	3857(9)	6205(2)	7688(3)	51(1)
C(6)	5787(6)	3562(2)	7885(2)	32(1)
C(7)	1424(7)	2149(2)	10189(2)	36(1)
C(8)	2177(9)	1237(2)	9976(3)	45(1)
H(3)	209(6)	505(2)	899(3)	35(7)
H(4)	600(7)	517(2)	725(3)	39(7)
H(5A)	238(7)	641(2)	819(3)	47(8)
H(5B)	490(9)	658(2)	713(3)	70(10)
H(7A)	−58(6)	223(2)	1014(2)	21(6)
H(7B)	214(6)	231(2)	1093(3)	39(8)
H(8A)	454(8)	114(2)	998(3)	56(9)
H(8B)	97(8)	90(2)	1048(3)	57(9)
H(8C)	135(7)	100(2)	928(3)	54(10)

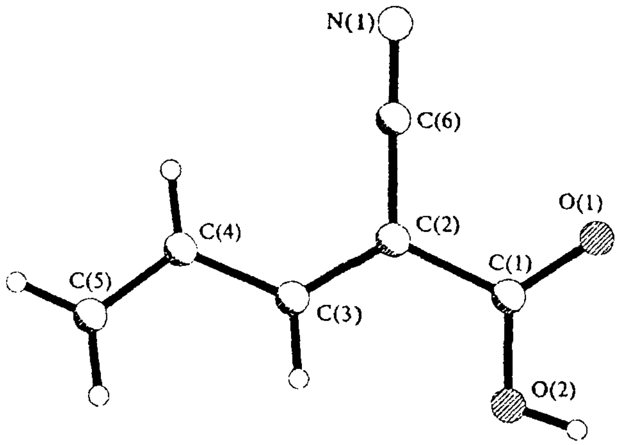


Fig. 1. The structure of molecule **1**.

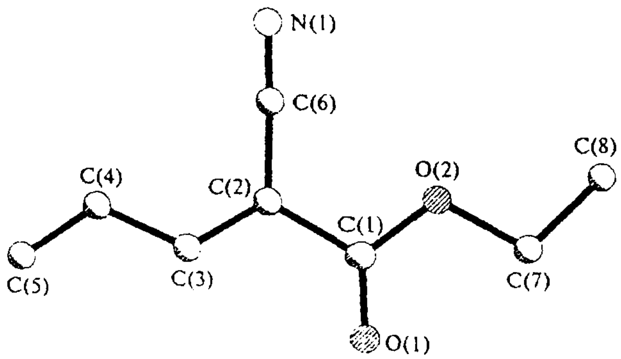
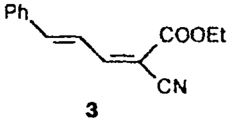


Fig. 2. The structure of molecule **2** (no hydrogen atoms are shown).

ecules **1** and **2** are equal within the limits of experimental error. Comparison of the geometry of molecule **2** and that of ethyl-2-cyano-5-phenyl-(2*E*,4*E*)-pentadienoate[10] (**3**) shows that the lengths of all corresponding bonds in these molecules are equal within the limits of experimental error, except for the C(7)—C(8) bond in the crystal of **3**, which is appreciably shorter than that in **2** (1.417(5) Å *vs.* 1.505(4) Å, respectively).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The ethyl group in molecule **2** has an eclipsed orientation with respect to the C(1)—O(1) bond (the C(7)—O(2)—C(1)—O(1) torsion angle is 1.3(3)°) and is in the anti-periplanar conformation (the C(8)—C(7)—O(2)—C(1) torsion angle is 173.9(3)°). In molecule **3**, this group has the same conformation, and the corresponding torsion angles are close to those found in **2**.

In crystals of **1** (Fig. 3), the molecules form centrosymmetric dimers due to the intermolecular hydrogen bond: the H(2O)...O(1)′ (1 − *x*, 2 − *y*, 1 − *z*) distance is 1.79 Å , the O(2)—O(1)′ distance is 2.622(4) Å, and the O(2)—H(2O)...O(1)′ angle is 172°; such dimers are absent (Fig. 4) in the crystals of **2**. Despite this fact, the crystal structures of **1** and **2** are similar; they consist of corrugated sheets that are nearly parallel to the *z*0*y* plane. The molecules of **1** in these sheets are bound due to the C—H...O intermolecular interaction, *viz.*, C(5)—H(5B)...O(1)″ (*x* − 1, 1.5 − *y*, −0.5 + *z*), the H(5B)...O(1)″ and C(5)...O(1)″ distances are respectively 2.62 Å and 3.40 Å , and the C(5)—H(5B)...O(1)″ angle is 140°. The molecules of **2** form centrosymmetric dimers due to analogous bonds, *viz.*, (1) C(3)—H(3)...O(1)′ (−*x*, 1 − *y*, 2 − *z*), the C(3)...O(1)′ and H(3)...O(1)′ distances are respectively 3.31 Å and 2.49 Å, and the C(3)—H(3)...O(1)′ angle is 155.7°; and (2) C(5)—H(5A)...O(1)′, the C(5)...O(1)′ and H(5A)...O(1)′ distances are respectively 3.474 Å and 2.60 Å, and the C(5)—H(5A)...O(1)′ angle is 149.5°.

The decisive effect of C—H...O interactions (in this case the H...O and C...O distances usually are in the range from 2.0 Å to 2.8 Å [11,12] and from 3.30 Å to 3.80 Å, respectively) on the packing motif in the crystal has been reported in the literature.[13,14] However, the nature of such interactions[15,16] is still under discussion; in particular, it is not clear whether they can be considered as weak hydrogen bonds. This is due to the fact that in most cases the O...H distances are appreciably longer than the sums of the van der Waals radii[9] (2.45 Å). An unambiguous answer to this question can be obtained from the analysis of the ED distribution in the crystal within the framework of the Bader topological theory.[17,18] The presence of the (3, −1) critical point in the interatomic area is a necessary and sufficient criterion for the existence of chemical (covalent, coordination, or hydrogen) bond.

Using the topological theory of the ED distribution, we analyzed the nature of the C—H...O interactions in crystals of **1** and **2**. For this purpose, the dimers of compounds **1** and **2** with different arrangements of interacting molecules (see Experimental) were studied. The ED distribution in such dimers (Table 5) was calculated by the HF/6-31G** quantum-chemical method using the non-optimized data of X-ray study.

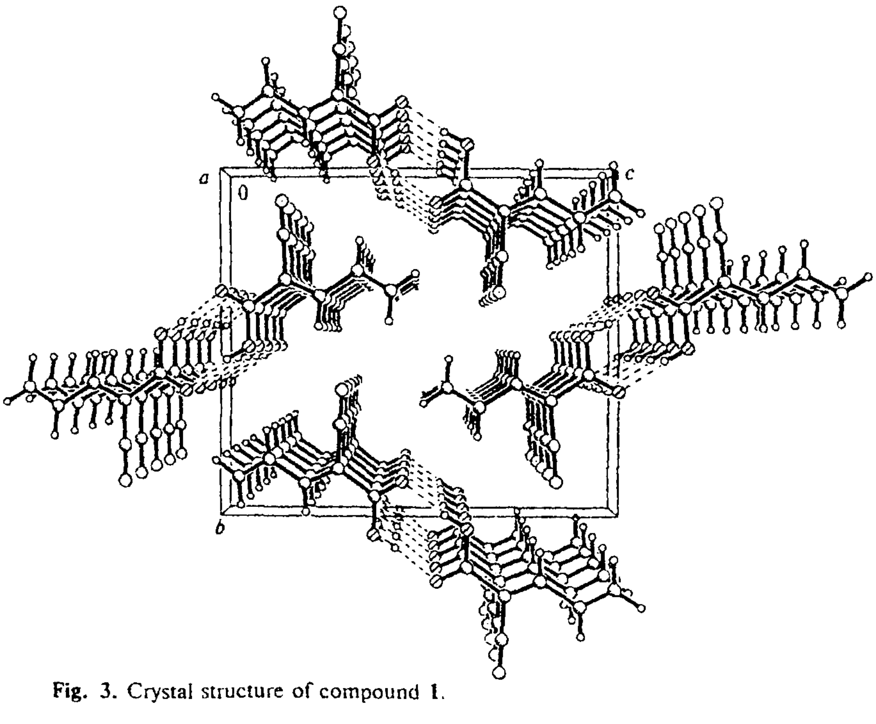


Fig. 3. Crystal structure of compound **1**.

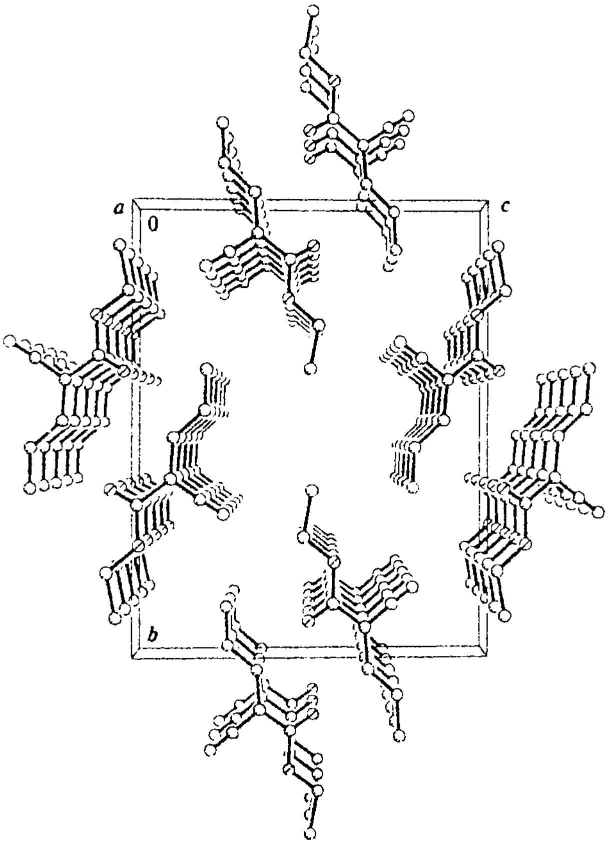


Fig. 4. Crystal structure of compound **2**.

Table 5. Topological characteristics of intermolecular interactions in critical (3, −1) points in dimers **1** and **2** according to *ab initio* HF/6-31G** calculations

Bond	λ_1	λ_2	λ_3	$\rho(r)$	$\nabla^2\rho(r)$
		$e\cdot Å^{-5}$		$/e\cdot Å^{-3}$	$/e\cdot Å^{-5}$
		Structure **1**			
H(2O)—O(1)′	−1.161	−1.124	5.617	0.222	3.332
H(5B)—O(1)″	−0.148	−0.136	0.919	0.041	0.635
C(2)—C(3)‴	−0.067	−0.043	0.498	0.038	0.388
C(4)—C(5)‴	−0.077	−0.049	0.496	0.039	0.370
		Structure **2**			
H(3)—O(1)′	−0.183	−0.174	1.111	0.050	0.754
H(5A)—O(1)′	−0.147	−0.142	0.904	0.042	0.614

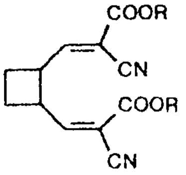
The (3, −1) critical points were found on all the C—H...O bonds in compounds **1**, **2**. The ED values at these points (see Table 5) are 0.05—0.04 e $Å^{-3}$, which is characteristic of this type of hydrogen bonds;[19,20] for the O—H...O bond, this value is appreciably larger (0.22 e $Å^{-3}$) and corresponds to the published data.[21] At the same time, the ED Laplacian $\nabla^2\rho(r)$ for such hydrogen bonds is positive, which makes it possible to consider these interactions as electrostatic type of bonding[22] or as the so-called interaction between closed shells.[17,19,21]

In addition to the sheets, the molecules in crystals of **1** and **2** form stacks by translating along the shortest crystallographic axis *a* (see Figs. 3 and 4). This leads to shortening of the C(2)...C(3)′ (1 + *x*, *y*, *z*) and C(4)...C(5)′ (1 + *x*, *y*, *z*) intermolecular contacts (3.40 Å and 3.39 Å, respectively) in **1** and the C(6)...C(1)′ (1 + *x*, *y*, *z*) intermolecular contact (3.23 Å) in **2**. However, the nature of these interactions in the crystals of **1** and **2** is fundamentally different. The (3, −1) critical points between interacting atoms were found in dimers **1** (see Table 5), which makes it possible to describe these contacts as weak bonds with predominant contribution of the electrostatic component. No such critical points were found in the crystals of compound **2**, which is likely an indication of the repulsive character of C...C contacts.

A stack structure formed by translating along the shortest crystallographic axis *c* (4.608(1) Å) was also found in crystal **3**; however, there are no sheets characteristic of compounds **1** and **2**, which is likely due to the relatively bulky phenyl substituent.

According to Schmidt,[23] this kind of stack structure is divided into three structural types (α, β, and γ) for which the length of the short crystallographic axis is >5.1 Å, 3.9±0.2 Å (arguments in favor of increasing the upper limit to 4.2 Å are adduced in Ref. 13), and 4.9±0.2 Å, respectively. These three groups have different reactivities in the solid phase. Thus, compounds **1** and **2** have β-structures while compound **3** has γ-structure. It is likely that the necessary condition for the formation of β-structure is the formation of planar or corrugated sheets in the crystal; in oxygen-containing compounds, they are stabilized by lateral C—H...O bonds.[13,24,25] It is likely that the shortened intersheet C...C contacts, which can be considered as electrostatic interactions, also favor the formation of β-structures. On the other hand, the available intermolecular shortened C...H, C...C, and H...H contacts result either in lengthening of the crystallographic axis along which the stacking occurs (*i.e.*, in α- and γ-structures[25]) or in the break of the stack structure.[26]

Particular interest in the β-type of packing is associated with the possibility for photochemical dimerization and polymerization reactions to occur in such crystals (if the corresponding fragments are available in the molecules). According to topochemical rules,[27] the reactions in question occur if the distances between the centers of the double bonds of neighboring molecules are in the range from 3.5 Å to 4.2 Å and the bonds are parallel (or almost parallel). The formation of β-structures (if stacks are formed by translation) always implies the fulfillment of these conditions since in this case the corresponding double bonds of the molecules in the stack are parallel and the distance between their centers in the neighboring molecules is equal to the length of the crystallographic axis along which the stacking occurs. Thus, it can be assumed that this type of photochemical reactions can occur in compounds **1** and **2**. Dimerization of molecules **1** and **2** can occur analogously to that observed for a number of carboxylic and dicarboxylic acids (1,3-butadiene derivatives),[27–29] *i.e.*, with the formation of dimer **4** as an end or intermediate product.



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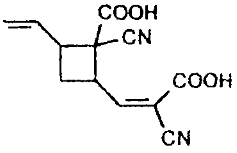

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However, one more route of dimerization of the molecules with the formation of dimer **5** exists for compound **1**, since the distance between the centers of the C(2)—C(3) and C(4)$'''$—C(5)$'''$ double bonds is 3.63 Å and the angle between them is 4.6°. Analogous dimerization in the case of crystal **2** is unlikely because the analogous distance is equal to 4.60 Å.

Thus, the possibility for topochemical reactions of compounds **1** and **2** to occur is due to the presence of β-structures in these crystals. These structures are stabilized due to intrasheet intermolecular C—H...O bonds and intersheet shortened C...C contacts that can be considered as electrostatic interactions.

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