Intermolecular Effects in Crystals of 11-(Trifluoromethyl)-15,16-dihydrocyclopenta[a]phenanthren-17-one

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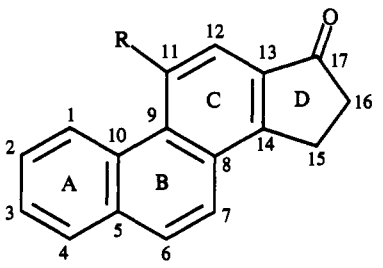
Abstract: The importance of C—F···H—C interactions in aligning molecules of the 11-trifluoromethyl derivative of cyclopenta[*a*]phenanthren-17-one in the crystalline state has been investigated by a comparison of the crystal structures of the 11-trifluoromethyl derivative with those of the previously reported 11-methyl and unsubstituted analogues. In the crystal structure of the 11-fluoro compound there are three C—F···H—C interactions and one C=O···H—C interaction per molecule, while for the methyl derivative one C=O···H—C interaction is all that serves to align molecules, and the molecular packing is different from that of the 11-trifluoromethyl derivative. These results imply that such weak intermolecular interactions are important in aligning molecules when stronger interactions such as O—H···O hydrogen bonds are not possible, and that such interactions are similar in importance to the ring–ring interactions that result in a 7.5 Å unit-cell dimension. The arrangements of interactions in each crystal structure have been highlighted by the use of graph-set analysis. The graph-set description of the packing of the 11-trifluoromethyl derivative in crystals may be described as $N_1 = R_2^2(14), R_2^2(14), C(9), R_2^2(16), C(7), C(8), C(8)$. With respect to the C–H···O interactions in the 11-methyl and the unsubstituted hydrocarbon the graph-set analyses are C(7) and C(11) respectively, compared with the C(8) in the 11-trifluoromethyl derivative. Thus, for each compound, the hydrogen atom involved in the C—H···O interaction is different. The molecular structure of the 11-trifluoromethyl derivative of cyclopenta[*a*]-phenanthren-17-one shows bay-region distortions similar to that found in the analogous 11-methyl derivative. The molecular geometry of the 11-trifluoromethyl compound was compared with that for the same ring system with an electron-donating CH_3 substituent replacing the electron-withdrawing CF_3 group. The crystal structure of the unsubstituted compound is also used in the comparison. It is found that for the trifluoro derivative there is a lengthening of the bonds in the bay region and also of the bond adjacent to the site of substitution. Other bonds acquire, as a result, more double-bond character.

Introduction

It is well-established that bay-region methyl substitution in the nonbenzo ring of phenanthrene-based polycyclic aromatic compounds often gives rise to carcinogenicity. Thus, in the cyclopenta[*a*]phenanthrene series, the ketone [15,16-dihydrocyclopenta[*a*]phenanthren-17-one (**1a**)] shown in Figure 1 is inactive in this regard, whereas its 11-methyl homologue (**1b**) is a potent carcinogen, the activity of which is similar to benzo[*a*]pyrene in a mouse skin assay.[1] The 11-ethyl 17-ketone (**1c**) is much less active, and further lengthening of the side-chain at the 11 position abolishes carcinogenicity.[2] The 11-methoxy analogue (**1d**) is also carcinogenic, although less so than **1b**, and in a similar manner, activity is lost with longer alkyl chains replacing the methoxy groups. Perhaps rather unexpectedly, the 11-phenol (**1e**) is also a carcinogen.[3] It is therefore apparent that the introduction of *small* substitutions at C11 in the parent ketone leads to carcinogenicity in this polycyclic aromatic series.

All these substituents are, however, electron-releasing, so it was of interest to examine the effect of substitution of a small electron-withdrawing group at this position. The trifluoromethyl group was selected because it is not much larger than a methyl group (van der Waals radii in Å; Pauling,[4] 1.2 for H and 1.35 for F; Bondi,[5] 1.2–1.45 for H and 1.5–1.6 for F), yet differs drastically in its electron affinity (0.8 eV for H and 3.5 eV for F, in the gas phase at 0 K). This compound [15,16-dihydro-11-(trifluoromethyl)cyclopenta[*a*]phenanthren-17-one (**1f**)] has therefore been synthesized,[6] and its *in vitro* metabolism and behavior in the Ames test have been investigated.[7] Like its 11-methyl analogue (**1b**), metabolism yields 1,2- and 3,4-dihydro diols, as well as the product of hydroxylation at C-15 in the five-membered ring. The compound itself is moderately mutagenic in the Ames test with *Salmonella typhimurium* TA 100 following metabolic activation. Of its metabolites only the 3,4-dihydro diol is mutagenic, and indeed it is almost three times more so than the original compound. Recent ^{32}P-postlabeling experiments have, however, shown little evidence of the formation of DNA



1a, R = H
1b, R = CH_3
1c, R = C_2H_5
1d, R = OCH_3
1e, R = OH
1f, R = CF_3

Figure 1. The cyclopenta[*a*]phenanthren-17-ones.

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adducts from the trifluoro derivative (**1f**) although such adducts are readily demonstrated for the 11-methyl analogue (**1b**);[8] DNA adducts of the latter have been previously studied in detail by a HPLC technique.[9] While the trifluoromethyl compound is shown to be mutagenic, tests of its carcinogenicity have not yet been completed.

In a previous X-ray diffraction study[10,11] it was established that, whereas the parent 17-ketone (**1a**) is essentially planar, the substituent in the 11-methyl derivative (**1b**) twists ring-A out of the plane of the other rings resulting in a bay region [C1–C10–C9–C11] torsion angle of 13.5°. Since CF_3 and CH_3 are similar in size, it was to be expected that their three-dimensional structures would also be similar, and this was supported by the observed ^{13}C NMR coupling constant.[6] In this paper the results of an X-ray crystal structure determination of the trifluoromethyl compound are reported and they quantify this expectation. The significance of C–H···O and C–H···F interactions is also the subject of study.

Experimental Section

The crystal of the trifluoromethyl compound (**1f**) chosen for X-ray data collection was 0.25 × 0.05 × 0.05 mm in size, the largest crystal available. X-ray diffraction data were measured with a Mo Kα (λ = 0.7107 Å) rotating anode source at 50 kV and 55 mA with a graphite monochromator using the Enraf Nonius FAST area detector diffractometer. The MADNES[12] software package was used for both data collection and processing. In all there were five different settings of the crystal at a crystal-to-detector distance of 42 mm with an offset angle of 30° in θ. Each data frame was measured for 30 s over an oscillation range of 0.2°. Those data frames that had counts in any pixel exceeding 32 767 were remeasured with the detector gain set at a lower value. This procedure allowed for the full range of intensities to be measured. In all, 13 105 reflections were measured and integrated. The program XSCALE[13] was used to give 2383 unique data to a *d*-spacing of 0.83 Å ($\sin\theta/\lambda$ = 0.602 Å^{-1}). The value of $R_{merge}(I)$ = 0.086. The measurement of the unit cell parameters was carried out by averaging the values obtained at regular intervals during the processing of the data. The crystal-to-detector distance was previously calibrated using a crystal of basic beryllium acetate which is cubic with a = 15.735 Å, as previously determined in this laboratory using a 4-circle diffractometer. When measured in this way, the unit cell parameters are a = 17.721(9) Å, b = 7.544 Å, c = 19.806 Å, and β = 97.84(2)°. The space group was determined to be $C2/c$ or Cc from the systematic absences in the X-ray diffraction pattern and was shown by the structure determination to be $C2/c$.

The crystal structure was solved by direct methods using the MULTAN 88 suite of program.[14] The structure refinement was based on F^2 values for all data except reflections with large negative values (which were omitted). In-house computer programs were used.[15] Atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[16] Hydrogen atoms were located from difference electron-density maps. The final atomic coordinates and the displacement parameters (average B_{eq} and U_{eq} with the estimated standard deviations) are given in Table 1. The individual anisotropic atomic displacement parameters are given in the supplementary material (deposited Tables A and B). Refinement statistics and final R values [R = 0.04 for $F > 4\sigma(F)$] are given in the footnote to Table 1.

Table 1. Final Atomic Coordinates (esd), Average B_{eq} (esd), and U_{eq} (esd)[a]

atom	x	y	z	B_{eq} (Å^2)	U_{eq} (Å^2)
C(1)	0.8842(1)	0.1760(3)	0.3323(1)	3.9(1)	0.050(1)
C(2)	0.9178(1)	0.1796(3)	0.3987(1)	4.7(1)	0.059(2)
C(3)	0.8759(1)	0.1417(3)	0.4512(1)	5.3(1)	0.067(2)
C(4)	0.8004(1)	0.1056(3)	0.4365(1)	4.9(1)	0.062(2)
C(5)	0.7642(1)	0.1053(3)	0.3688(1)	3.6(1)	0.046(1)
C(6)	0.6837(1)	0.0842(3)	0.3564(1)	4.4(1)	0.056(1)
C(7)	0.6468(1)	0.1002(3)	0.2934(1)	3.9(1)	0.050(1)
C(8)	0.6863(1)	0.1209(2)	0.2365(1)	3.09(9)	0.039(1)
C(9)	0.7674(1)	0.1234(2)	0.24384(9)	2.97(9)	0.038(1)
C(10)	0.8066(1)	0.1320(2)	0.3143(1)	3.17(9)	0.040(1)
C(11)	0.8021(1)	0.1152(2)	0.1824(1)	3.19(9)	0.040(1)
C(12)	0.7582(1)	0.1266(3)	0.1194(1)	4.0(1)	0.051(1)
C(13)	0.6795(1)	0.1405(3)	0.1138(1)	3.6(1)	0.045(1)
C(14)	0.6443(1)	0.1356(2)	0.1702(1)	3.29(9)	0.042(1)
C(15)	0.5586(1)	0.1462(3)	0.1532(1)	4.3(1)	0.054(1)
C(16)	0.5456(1)	0.1687(3)	0.0758(1)	5.2(1)	0.065(2)
C(17)	0.6224(1)	0.1519(3)	0.0520(1)	4.6(1)	0.059(2)
C(18)	0.8854(1)	0.0836(3)	0.1793(1)	4.1(1)	0.052(1)
F(1)	0.92867(6)	0.2303(2)	0.18755(7)	5.10(7)	0.0646(8)
F(2)	0.89761(7)	0.0170(2)	0.11859(6)	5.97(8)	0.0756(9)
F(3)	0.91721(6)	−0.0342(2)	0.22507(6)	4.71(7)	0.0596(8)
O(1)	0.6349(1)	0.1470(3)	−0.00680(9)	6.5(1)	0.082(1)
H(1)	0.912(1)	0.210(3)	0.294(1)	4.4(5)	0.056(7)
H(2)	0.970(1)	0.214(2)	0.410(1)	4.5(5)	0.057(7)
H(3)	0.899(1)	0.140(3)	0.497(1)	5.9(6)	0.075(8)
H(4)	0.767(1)	0.079(3)	0.474(1)	6.1(6)	0.077(8)
H(6)	0.659(1)	0.067(3)	0.394(1)	4.3(6)	0.054(7)
H(7)	0.595(1)	0.091(3)	0.284(1)	3.8(5)	0.048(6)
H(12)	0.783(1)	0.125(3)	0.079(1)	4.2(5)	0.053(7)
H(15A)	0.535(1)	0.042(3)	0.169(1)	5.5(6)	0.070(8)
H(15B)	0.538(1)	0.238(3)	0.179(1)	5.4(6)	0.069(8)
H(16A)	0.513(1)	0.074(3)	0.054(1)	6.5(6)	0.082(8)
H(16B)	0.527(1)	0.287(3)	0.061(1)	7.2(8)	0.092(9)

[a] B_{eq} = (1/3)[trace orthogonalized B_{ij} matrix]. U_{eq} = (1/3)[trace orthogonalized U_{ij} matrix]. $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ ($F > 4\sigma$) = 0.044 (1358 data). For all data (as refined) R_1 = 0.080; $wR_1 = \{\Sigma w(k|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$ = 0.045; number of data = 2149. $R_2 = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$ = 0.073; $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$ = 0.089; goodness of fit = $\{\Sigma[w(F_o^2 - F_c^2)]^2/(n-m)\}^{1/2}$ = 1.40. F_o = F observed; F_c = F calculated; $n - m$ = number of degrees of freedom. $F_o - F_c$ map: ρ_{max} = 0.25 e/Å^3, ρ_{min} = −0.27 e/Å^3.

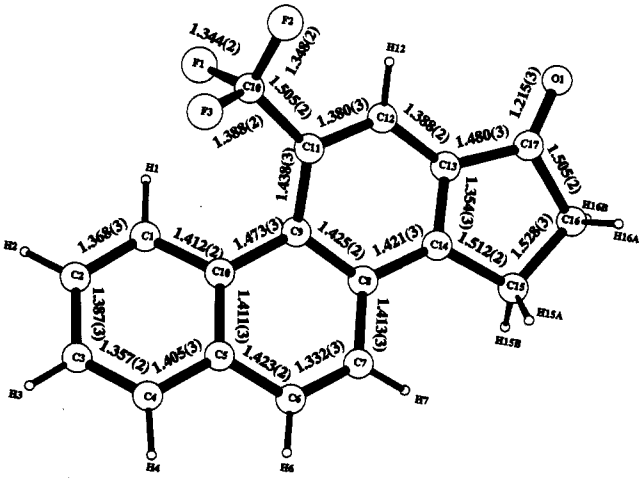

Figure 2. View of the 11-trifluoromethyl molecules with atom labeling and the corresponding bond lengths between non-hydrogen atoms.

Results and Discussion

(a) Comparisons of the Trifluoro Compound with the 11-Methyl and the Unsubstituted Compounds. The molecular structure of the trifluoromethyl compound (**1f**) is shown in Figure 2 with bond lengths between the non-hydrogen atoms (bond lengths are also given in deposited Table C). The corresponding angles are given in deposited Table D. A comparison of the molecular geometries of the 11-trifluoromethyl compound (**1f**), its 11-methyl

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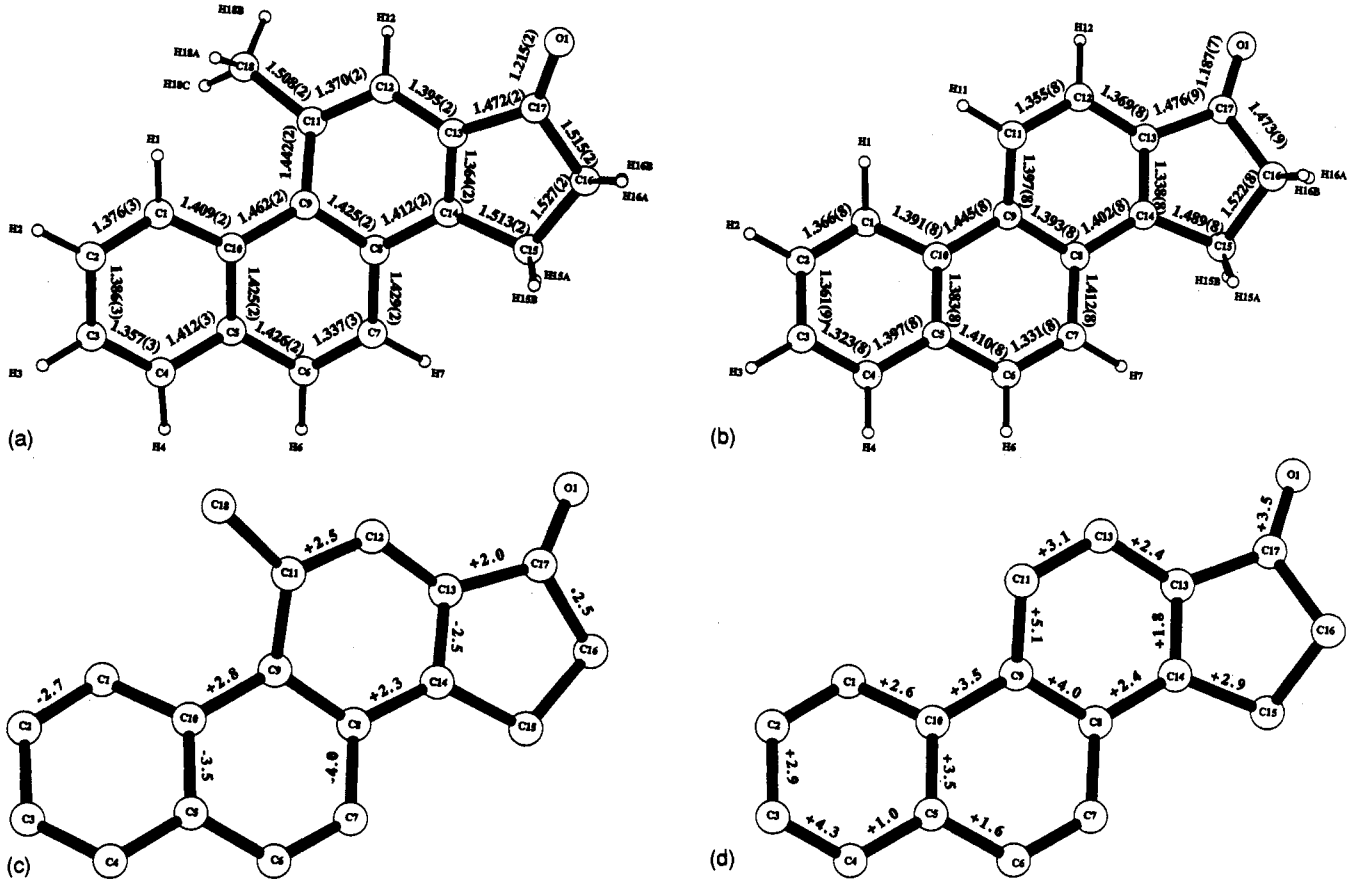

Figure 3. View of the two analogs, 11-methyl and unsubstituted, and the difference in their bond lengths: (a) the 11-methyl molecule; (b) the unsubstituted molecule; (c) the difference in bond lengths between the 11-trifluoromethyl and the 11-methyl molecule as a multiple of the esd; and (d) the difference in bond lengths between the 11-trifluoromethyl and the unsubstituted molecule as a multiple of the esd. The difference in bond length was calculated by subtracting the value of the bond length of the analog from the corresponding value of the 11-trifluoromethyl molecule. The esd values used for parts c and d are calculated using the equation $\sigma^2(\Delta) = \sigma^2(d_1) + \sigma^2(d_2)$, where d_1 and d_2 are bond lengths being compared.

analogue (**1b**),[10,11] and the unsubstituted molecule[11] is shown in parts a and b of Figure 3, together with differences in the bond lengths of the non-hydrogen atoms. Only bond differences between the 11-trifluoromethyl compound and each of the analogues, 11-trimethyl and the unsubstituted compound, of up to 0.008 Å are shown in parts c and d of Figure 3. It is found that for the trifluoro derivative there is a lengthening of the C9–C10 bond of the bay region and also the C11–C12 bond adjacent to the site of substitution. Other bonds such as C5–C10, C7–C8, and C16–C17 then acquire more double-bond character. Selected torsion angles and their esd values (in parentheses) are given in Table 2 for the three derivatives. The complete list of torsion angles of the three derivatives is given in deposited Table E. The major distortions are indicated by asterisks. Changes in the planarity of the ring systems in the three compounds are illustrated in Figure 4. The angle between the planes of ring A and ring D increases as the substituting atom becomes larger, 2.92, 11.98, and 17.03° for H to CH_3 to F, respectively.

(b) Crystal Packing and Hydrogen-Bond Analysis. In the crystal structure of the 11-trifluoromethyl compound the molecules are stacked along the *b* direction, as shown in Figure 5.

Each 11-trifluoromethyl molecule has four groups (the three fluorine atoms and one carbonyl oxygen atom) that are potential hydrogen-bond acceptors. The interatomic distances are given in Table 3. A graph-set analysis of the hydrogen-bond system, according to the procedures described by Etter, MacDonald, and Bernstein,[17-19] reveals an interesting three-dimensional network involving hydrogen atoms. The different motifs in the first level, i.e., all the different types of hydrogen bonds, are shown in Figure 6 (**R** = ring, a finite ring motif; **C** = chain, infinite chain motif). The full description is:

$$N_1 = \mathbf{R}_2^2(14), \mathbf{R}_2^2(14), \mathbf{C}(9), \mathbf{R}_2^2(16), \mathbf{C}(7), \mathbf{C}(8), \mathbf{C}(8)$$

The first two finite ring motifs (in Figure 6a), $\mathbf{R}_2^2(14)$ and $\mathbf{R}_2^2(16)$, are formed by interaction of the F1 atom. The next two motifs (in Figure 6b), the infinite chain **C**(9) and the finite ring $\mathbf{R}_2^2(16)$, are formed by interactions of the fluorine atom F2. The next two infinite motifs (in Figure 6c), **C**(7) and **C**(8), are formed by interactions of the fluorine atom F3. In addition to these interactions involving fluorine atoms F1 to F3, there is an infinite **C**(8) motif involving a C–H···O interaction with a carbonyl oxygen atom (see Figure 6b). Altogether there are seven different types of these interactions, three finite and four infinite.

A graph-set analysis at a higher level is shown in Figure 7, i.e., a combination of more than one type of hydrogen bond. The patterns of the higher levels in addition to the first level are summarized in Table 4. Molecules pack by stacking (Figure 5), and from the graph-set analysis of the hydrogen bonds, it is evident that binding interactions of F1, F2, and O1 are responsible for the infinite two-dimensional hydrogen-bound network in plane *ac* (Figure 7, a and b), and the F3 binding interaction is the one that is turning the hydrogen bond network into a three-dimensional one (Figure 7c). The fact that the crystal displays an infinite

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Table 2. Torsion Angle Values of the Three Derivatives: 11-Trifluoromethyl, 11-Methyl, and the Unsubstituted

Central Bond	11-trifluoro-methyl	11-methyl[a]	unsubstituted[a]
C1–C2			
C3–C2–C1–C10	–0.8(3)	1.0(3)	1.8(3)
C1–C10			
C2–C1–C10–C5	4.7(3)	4.6(3)	–2.0(3)
C2–C3			
C1–C2–C3–C4	–1.8(3)	–4.6(3)	–0.6(3)
C3–C4			
C5–C4–C3–C2	0.3(3)	2.4(3)	–0.2(3)
C4–C5			
C3–C4–C5–C10	3.9(3)	3.4(3)	–0.2(3)
C5–C6			
C7–C6–C5–C10	–4.1(3)	–1.5(3)	0.7(3)
C5–C10			
C6–C5–C10–C9	–4.9(3)	–5.4(3)[b]	0.5(3)
C4–C5–C10–C1	–6.2(3)[b]	–6.7(3)[b]	1.3(3)
C6–C7			
C5–C6–C7–C8	6.3(3)[b]	4.5(3)	–0.9(3)
C7–C8			
C6–C7–C8–C9	0.8(3)	–0.4(3)	–0.2(3)
C8–C9			
C10–C9–C8–C7	–9.4(3)[b]	–6.4(3)[b]	1.4(3)
C11–C9–C8–C7	–8.7(3)[b]	–6.3(3)[b]	0.9(3)
C8–C14			
C13–C14–C8–C9	4.3(3)	2.2(3)	0.3(3)
C15–C14–C8–C7	5.2(3)[b]	3.1(3)	–1.0(3)
C9–C10			
C5–C10–C9–C8	11.2(3)[c]	9.1(3)[b]	–1.6(3)
C1–C10–C9–C11	16.0(3)[c]	14.0(3)[c]	–2.6(3)
C9–C11			
C12–C11–C9–C8	7.7(3)[b]	5.9(3)[b]	–1.3(3)
C11–C12			
C9–C11–C12–C13	–2.1(3)	–1.5(3)	0.4(3)
C12–C13			
C14–C13–C12–C11	–2.8(3)	–2.8(3)	0.9(3)
C13–C14			
C12–C13–C14–C8	1.7(3)	2.4(3)	–1.3(3)
C17–C13–C14–C15	–0.9(3)	0.2(3)	–1.0(3)
C13–C17			
C16–C17–C13–C14	4.5(3)	0.4(3)	6.1(3)[b]
O1–C17–C13–C12	1.8(3)	–1.6(3)	3.8(3)
C14–C15			
C16–C15–C14–C13	–2.9(3)	–0.6(3)	–4.3(3)
C15–C16			
C17–C16–C15–C14	5.4(3)[b]	0.8(3)	7.9(3)[b]
C16–C17			
C15–C16–C17–C13	–6.1(3)[b]	–0.7(3)	–8.5(3)[b]

[a] Torsion angles for the 11-methyl and the unsubstituted derivatives are for the enantiomer of the published one. [b] Torsion angle values between |5°| and |10°|. [c] Torsion angle value greater than |10°|.

three-dimensional hydrogen bond network may possibly contribute to its physical properties,[20] such as its heat of sublimation.

This analysis has highlighted the significance of C–F···H–C interactions which, although weak, contribute significantly to the alignment of molecules in the crystalline state and are probably as important as ring–ring interactions. In our recent study[21] on intermolecular hydrogen bonding involving a carbon-bound fluorine atom as an acceptor, we found that, in the presence of an additional acceptor such as an oxygen atom, the mean H···F distance is 2.5(1) Å when a CF_3 group is attached to an aromatic ring. While this is shorter than the value found in 11-(trifluoromethyl)-17-ketocyclopenta[*a*]phenanthrene (2.8 Å), it is probably well within the expected range.

The carbonyl oxygen in the trifluoro derivative is involved in an interaction with an aromatic hydrogen atom, C—H···O=C, with a H···O distance of 2.62 Å. This is longer than the value reported by Taylor and Kennard,[22] 2.0–2.4 Å. A comparison of

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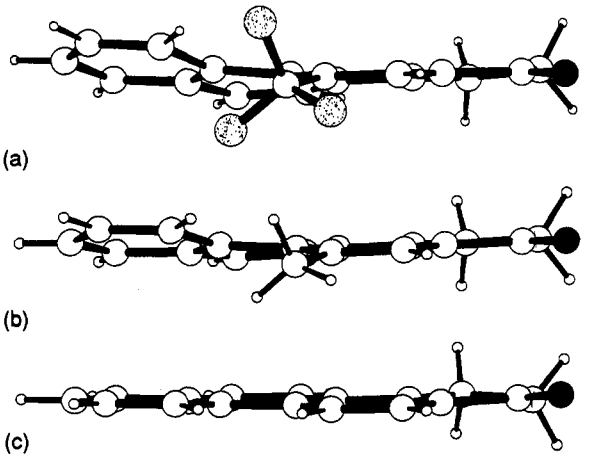

Figure 4. Comparison of the planarity of the three molecules: (a) the 11-trifluoromethyl compound; (b) the 11-methyl compound; and (c) the unsubstituted compound. All the structures are drawn along the plane of the five-membered ring.

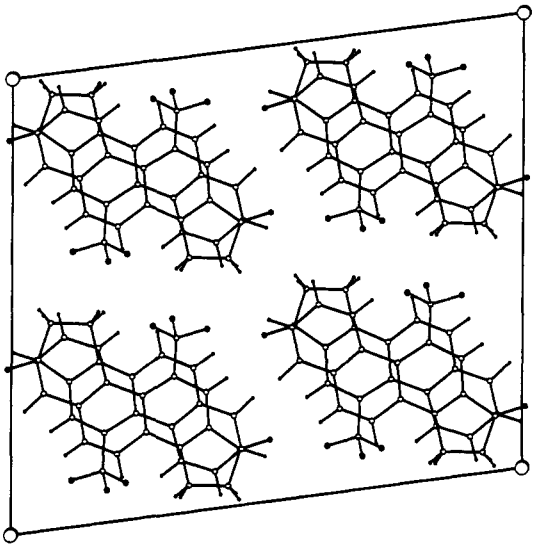

Figure 5. Crystal packing of the 11-trifluoromethyl compound (**1f**), view down the *b* axis (7.544 Å).

Table 3. F(O)···H Bond Distances in C–F(O)···H–C Interactions

molecule	inter-action	distance (Å)	figure
(a) 11-trifluoromethyl	F1···H1	2.80	6a, 7a
	H2	2.81	6a, 7a
	F2···H3	2.69	6b, 7b
	H2	2.92	6b, 7b
	H3···H15	2.60	6b
	H7	2.84	6c, 7c
	O1···H6	2.62	6b, 7b
(b) 11-methyl	O1···H7	2.49	
(c) unsubstituted	O1···H3	2.50	

the C—H···O=C interaction (distances and graph-set motifs of the 11-methyl analog and the unsubstituted molecule) is given in Table 5. The graph-set analyses of the 11-methyl derivative and of the unsubstituted cyclopentaphenanthrene are, of course, totally different because there is only one hydrogen-bond acceptor, the 17-ketone group. We see that the absence of an additional acceptor, such as a fluorine atom, affects both the C–H···O distance, causing it to be shorter, and the graph-set motif. The ability of carbon-bound hydrogen atoms to act as proton donors in hydrogen-bond-like interactions was first pointed out by Sutor.[23] It was the subject of controversy, but is more accepted today, as

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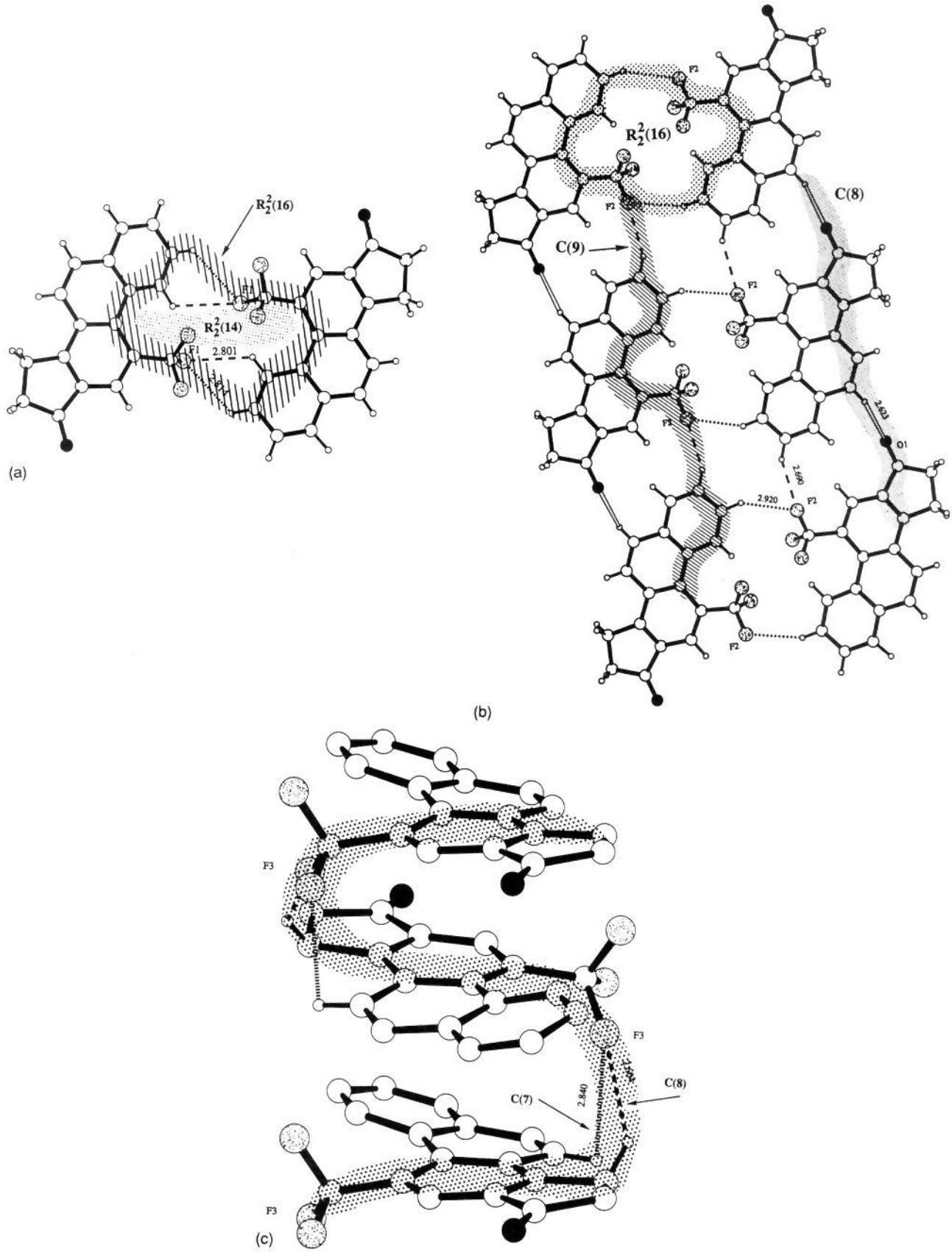

Figure 6. The seven different types of hydrogen bonds present in the hydrogen bond network of the 11-trifluoromethyl compound: (a) $\mathbf{R}_2^2(14)$ and $\mathbf{R}_2^2(16)$ motifs formed by F2 interactions; (b) **C**(9) and $\mathbf{R}_2^2(16)$ motifs formed by F2 interactions and **C**(8) formed by O1 interactions; and (c) **C**(7) and **C**(8) motifs formed by F3 interactions (to simplify the picture, the nonparticipating hydrogen atoms are not shown). The different types of hydrogen bonds are drawn in a different manner, and the atoms participating in each motif are highlighted with different styles of shading. In part c, to simplify the diagram, only the trend of the two motifs, which is a snake-like shape, has been shaded.

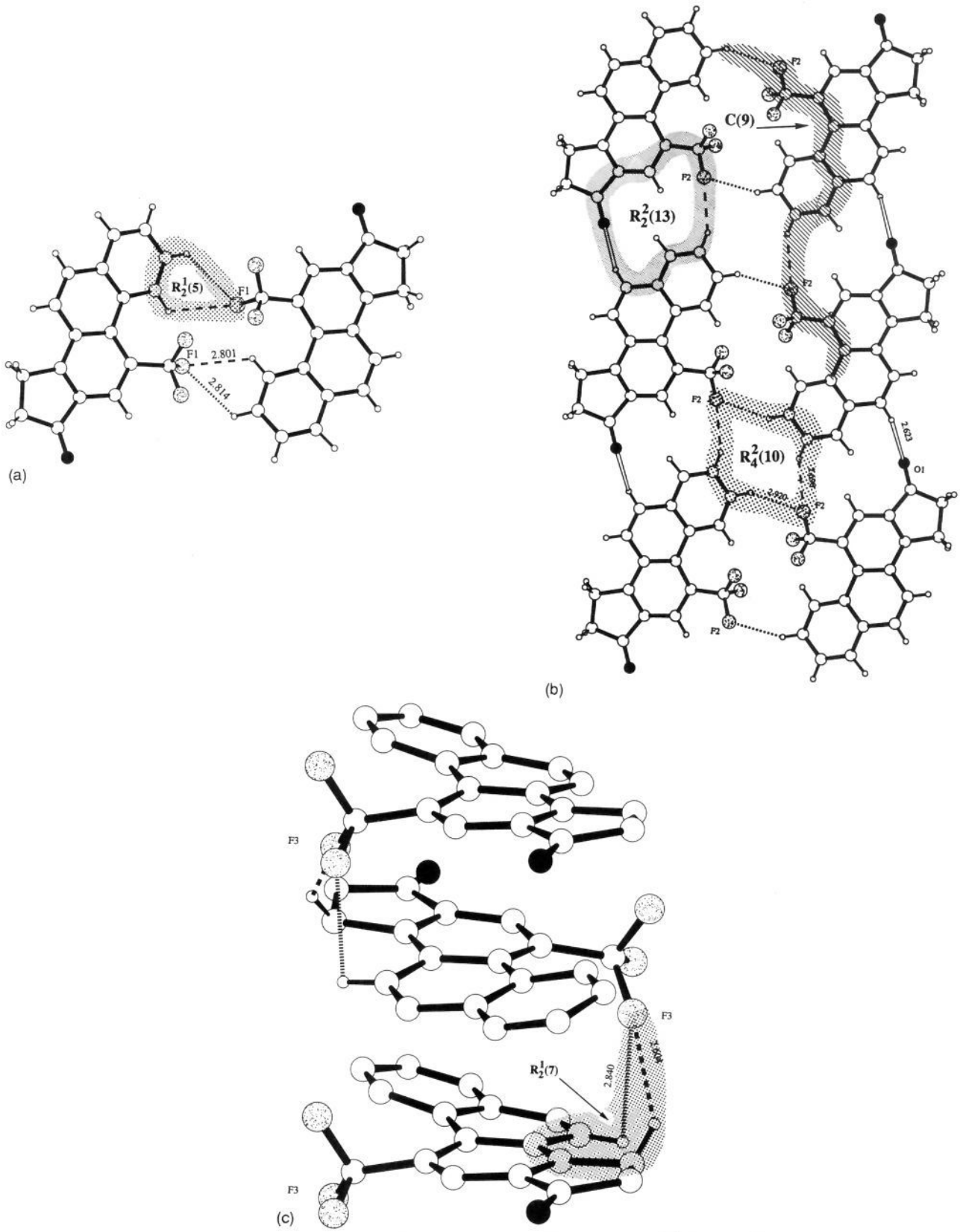

Figure 7. Patterns in the higher levels of graph-set analysis of the 11-trifluoromethyl compound: (a) $\mathbf{R}_2^1(5)$ pattern formed by two F1 interactions; (b) **C**(9) and $\mathbf{R}_4^2(10)$ patterns each formed by F2 interactions and $\mathbf{R}_2^2(13)$ pattern formed by a combination of F2 and O1 interactions; and (c) $\mathbf{R}_2^1(7)$ pattern formed by F3 interactions.

a result of studies by Taylor, Kennard, Desiraju, and others[22-27] on the crystallographic evidence for the existence of C–H···O interactions. Desiraju[25] noted that "C–H···O bonds...need to be considered as important contributors in the formation of hydrogen-bond patterns in organic crystals." We arrive at the same conclusion regarding the C–H···F interactions based on our

Table 4. Graph-Set Analysis to the 6th Level of the Hydrogen Bond Network

level	graph-set notation	acceptor atoms involved
N_1	$R_2^2(14)$, $R_2^2(16)$, C(9), $R_2^2(16)$, C(7), C(8), C(8)	F1, F2, F3, and O1
N_2	$R_2^1(5)$	F1
N_3	C(9)	F2
N_4	$R_2^1(7)$	F3
N_5	$R_4^2(10)$	F2
N_6	$R_2^2(13)$	F2 and O1

Table 5. C—H···O═C Distance and Graph-Set Notation of 11-Trifluoromethyl, 11-Methyl, and Unsubstituted Compounds

compd	H···O distance (Å)	graph-set motif
11-trifluoromethyl	2.62	C(8)
11-methyl	2.49	C(7)[a]
unsubstituted	2.50	C(11)[a]

[a] Not included in the figures.

studies.[21] The combination of these two types of interactions, C–H···O and C–H···F, gives rise to the three-dimensional hydrogen-bond network in the crystal structure under study.

Conclusions

The steric overcrowding of an 11-methyl group is enhanced when the hydrogen atoms of the methyl group are replaced by fluorine atoms. Thus, the larger the substituent group at the 11 position, the greater the twist of the entire molecule as a result of steric overcrowding. This twist is particularly evident between rings B and C (Figure 1).

The three cyclopentaphenanthrenone compounds with trifluoromethyl, hydrogen, or methyl substituents in the 11 position each stack in the crystalline state along the *b* axis, which is of the order of 7.5 Å in each crystal structure (caused, presumably, by ring–ring interactions). A graph-set analysis of the crystal structure of the trifluoro derivative, which does not contain any hydroxyl or amino groups that could be strong hydrogen-bond donors, shows that there is a three-dimensional network of C—H···O═C and C—H···F—C interactions which can be considered as weak hydrogen bonds. The linearity of most of these interactions led us to suggest again[21,27] that C–H···O and C–H···F interactions play a significant role in the alignment of these (and other) molecules in the crystalline state.

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Supplementary Material Available: Tables of crystallographic data, interbond angles, torsion angles (of the additional two compounds, 11-methyl substituted and unsubstituted), and anisotropic displacement parameters (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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