Supporting Information

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Structural, spectroscopic, Hirshfeld surface and DFT spproach of 3,9-dibromophenanthrene

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S1 : Synthesis and NMR Data

*Synthesis of 3,9-Dibromophenanthrene (**2**)*

The reagents used in the reactions were supplied commercially by Aldrich and Merck.

To a solution of 9-bromophenanthrene (**1**) (1.0 g, 3.89 mmol) in dichloromethane (7 mL) at -18 °C, molecular bromine (0.475 g, 2.97 mmol,1.1 eq) was added via syringe. The mixture was allowed to stand at -18 °C, protected with a drying tube (containing blue silica gel and NaOH), until consumption of the molecular bromine (13 d).

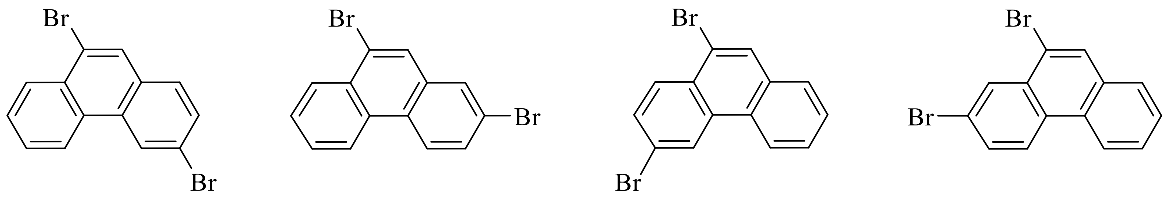
The solvent and unreacted bromine was evaporated under reduced pressure. The crude product was subjected to recrystallization procedures in a mixture of CH_2Cl_2 / hexane (5 mL: 2 mL) at room temperature. Crystals that formed after one day were collected as white needles (169 mg, 13% yield). Further attempts to obtain more crystals from the supernatant was unsuccessful.

*3,9-Dibromophenanthrene (**2**):* White needle crystals, Yield 13%. m.p.: 144-146 ºC (lit. m.p. 143.5 °C[6] and 144-145 °C[7]). R_f = 0.73 (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.61- 8.58 (m, 1H), 8.39- 8.37 (m, 1H), 8.06 (s, 1H), 7.76-7.66 (m, 4H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ131.2, 130.7, 130.6, 130.4, 130.1, 129.9, 129.2, 128.19, 128.17, 127.8, 125.7, 122.9, 122.2, 121.3. IR (ν_{max}, cm^{-1}): 2360, 1583, 1482, 1404, 1082, 1016, 914, 875, 856, 806, 748, 713. GC/MS m/z: 334/336/338 $[M-2H]^+$, 256 $[M-Br]^+$, 176 $[M-2Br]^+$.

The ^{1}H-NMR, ^{13}C-NMR, and ^{1}H-NMR spectra of the crude product and the title compound were recorded and displayed in Figures. S1, S2 and S3, respectively.

The molecular structures and ratios of the other compounds in the crude product were determined by using the NMR values of the known dibromphenantrenes and 3,9-dibromophenanthrene (**2**). According to ^{1}H-NMR analysis of the crude product, we observed a mixture of 3,9-dibromophenanthrene (**2**), 1,9-dibromophenanthrene (**3**) and 9,10-dibromophenanthrene (**4**) in approximately 1:1:0.4 ratio, with few or no starting compound. This ratio was determined from the relative area of the signals at δ 8.05, 7.90 and 8.50 in the ^{1}H-NMR spectrum (Fig. S1). The ^{1}H-NMR spectrum exhibited the expected aromatic signals for the three dibromides. Two doublets at δ 7.90 and δ 8.63 and a triplet at δ 7.51 agree with the ortho substitution on A ring of the phenanthrene of the 1,9-dibromophenanthrene **3**. In addition, we could distinguish the signal of the other aromatic protons in 1,9-dibromophenanthrene (**3**) at δ 8.68-8.66 (m), δ 8.59 (s), δ 8.43-8.40 (m) and δ 7.77-7.65 (m). The formation of 9,10-dibromophenanthrene (**4**) could be confirmed by crude product's ^{1}H-NMR spectrum, where the signals of the aromatic protons appear at δ 8.68-8.66 (m), δ 8.51-8.49 (m) and, δ 7.77-7.65 (m). These values are consistent with literature values.[18]

The ^{1}H-NMR and ^{13}C-NMR spectroscopic data of the 3,9-dibromophenanthrene (**2**) are in good agreement with 9-bromophenanthrene (**1**). Since the signal seen at δ 8.06 ppm shows a close value with the peak seen as δ 8.10 in 9-bromphenanthrene (**1**), it can be thought to belong to H_{10}. There is another singlet in the spectrum. Accordingly, the structures will belong to one of the structures shown in Scheme 2. When we examine the spectrum of 9-bromphenanthrene (**1**), it is seen that H_5 and H_8 protons in the ring sharing the same space as brom give multiplet and the signal of H_8 proton shifts to a very low field due to the γ-gauche effect of bromine. However, H_1 and H_4 in the other ring are observed as doublets. This observation is consistent with structure A. Because we can say that two multiplets at δ 8.39-8.37 and δ 8.61-8.58 ppm were attributed to the protons in the ring (H_5 and H_8) that share the same space with bromine. H_4 resonated as a singlet at δ 8.78. Because of the γ-gauche effect between H_4 and H_5, H_4 gives a signal in the lower field (δ 7.76-7.66).



A **B** **C** **D**

Scheme 1. The molecular structures of A, B, C, D.

The ^{1}H-NMR values of 3-bromphenanthrene (**3**)[19] confirm our explanation, especially for H_1 and H_4 protons. Because, while the H_4 proton resonance at δ 8.70 ppm, the proton H_1 gives a signal at 7.83-727 ppm. The ^{13}C-NMR spectrum of (**2**) exhibited 14 signals, 6 of which are quaternary, in agreement with the proposed structure. The aromatic carbon atoms resonated at δ 131.2, 130.7, 130.6, 130.4, 130.1, 129.9, 129.2, 128.2 (128.19), 128.2 (128.17), 127.8, 125.7, 122.9, 122.2 and 121.3.

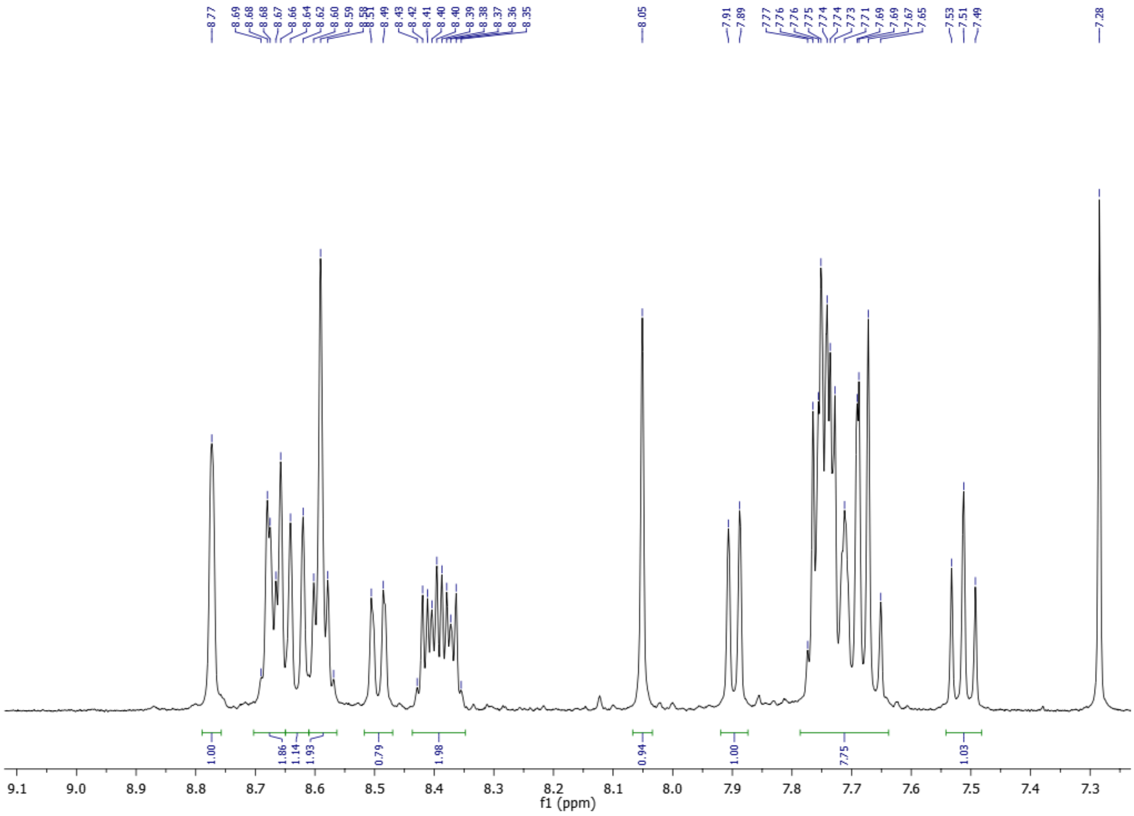


Figure S1 : [1]H NMR spectrum of the crude product (400 MHz, $CDCl_3$)

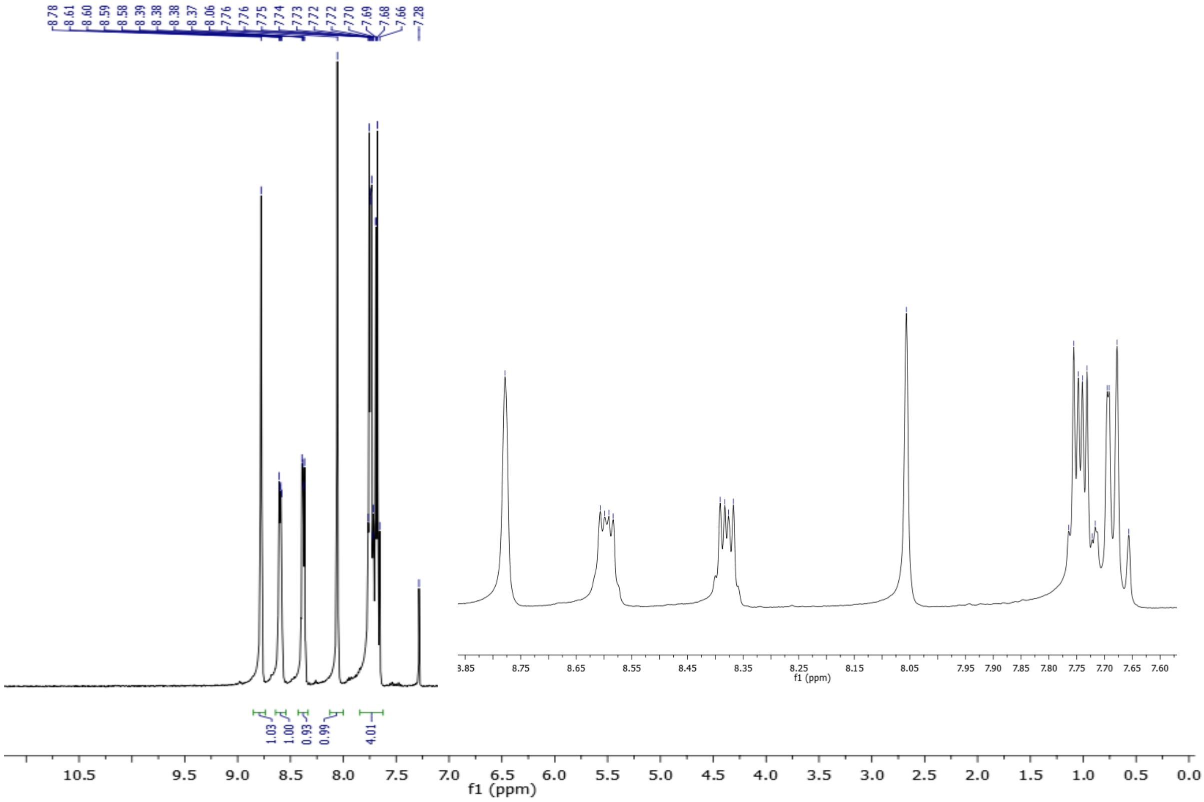


Figure S2 : ^{1}H NMR spectrum of 3,9-dibromophenanthrene (**2**) (400 MHz, $CDCl_3$)

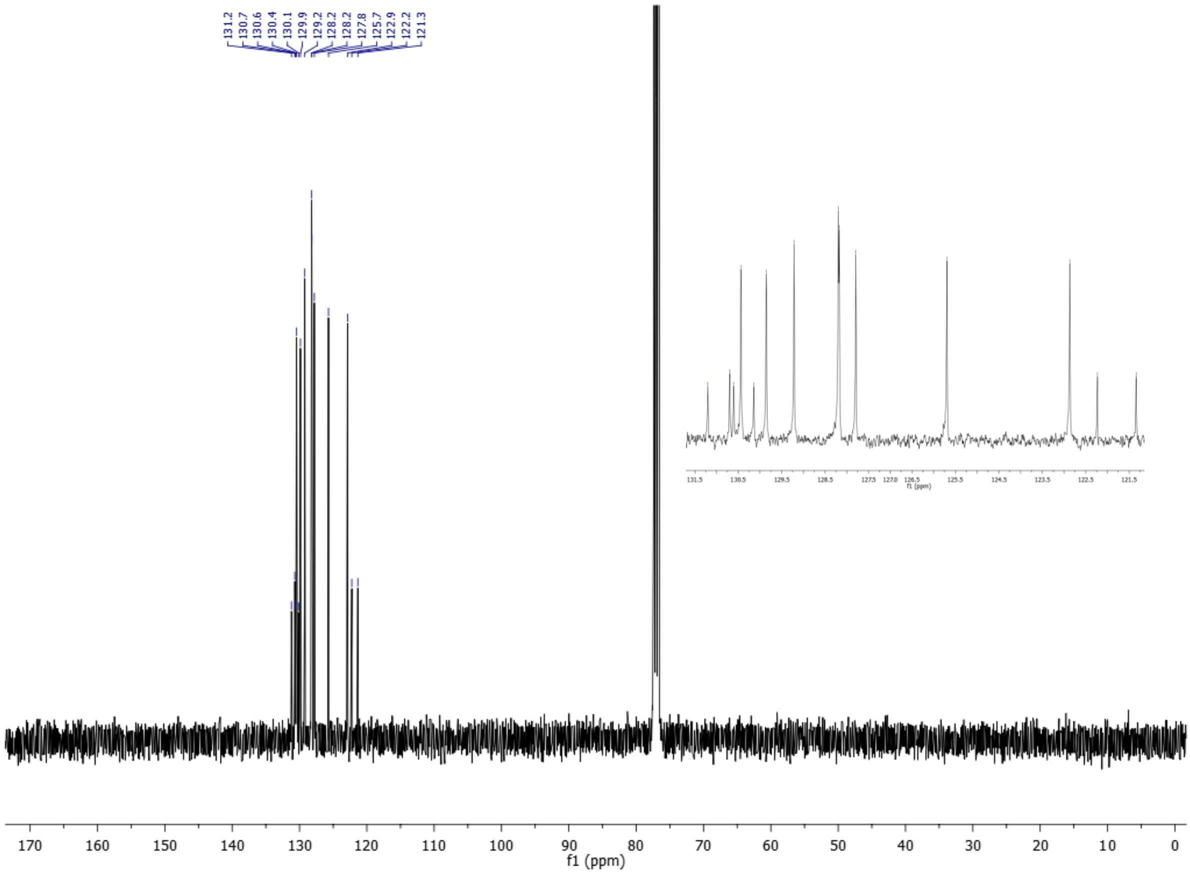


Figure S3 : ^{13}C NMR spectrum of 3,9-dibromophenanthrene (**2**) (100 MHz, $CDCl_3$)

S2: X-ray Crystallaographic Data

checkCIF (basic structural check) running

checkCIF/PLATON (basic structural check)

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: cem45_0m_a

Bond precision:	C-C = 0.0103 A		Wavelength=0.71073
Cell:	a=3.9624(11)	b=24.445(7)	c=11.825(4)
	alpha=90	beta=93.722(10)	gamma=90
Temperature: 296 K			

	Calculated	Reported
Volume	1143.0(6)	1143.0(6)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C14 H8 Br2	C14 H8 Br2
Sum formula	C14 H8 Br2	C14 H8 Br2
Mr	336.00	336.02
Dx,g cm-3	1.953	1.953
Z	4	4
Mu (mm-1)	7.057	7.057
F000	648.0	648.0
F000'	646.07	
h,k,lmax	5,30,14	5,30,14
Nref	2420	2420
Tmin,Tmax	0.387,0.460	0.573,0.745
Tmin'	0.358	

Correction method= # Reported T Limits: Tmin=0.573 Tmax=0.745 AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 26.780

R(reflections)= 0.0609(1618) wR2(reflections)= 0.1269(2420)

S = 1.162 Npar= 146

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds .... 0.01025 Ang.

Alert level G

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 8.15 Why ?
PLAT333_ALERT_2_G Large Aver C6-Ring C-C Dist. C1 -C10 1.42 Ang.
PLAT899_ALERT_4_G SHELXL97 is Deprecated and Succeeded by SHELXL 2017 Note

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
3 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

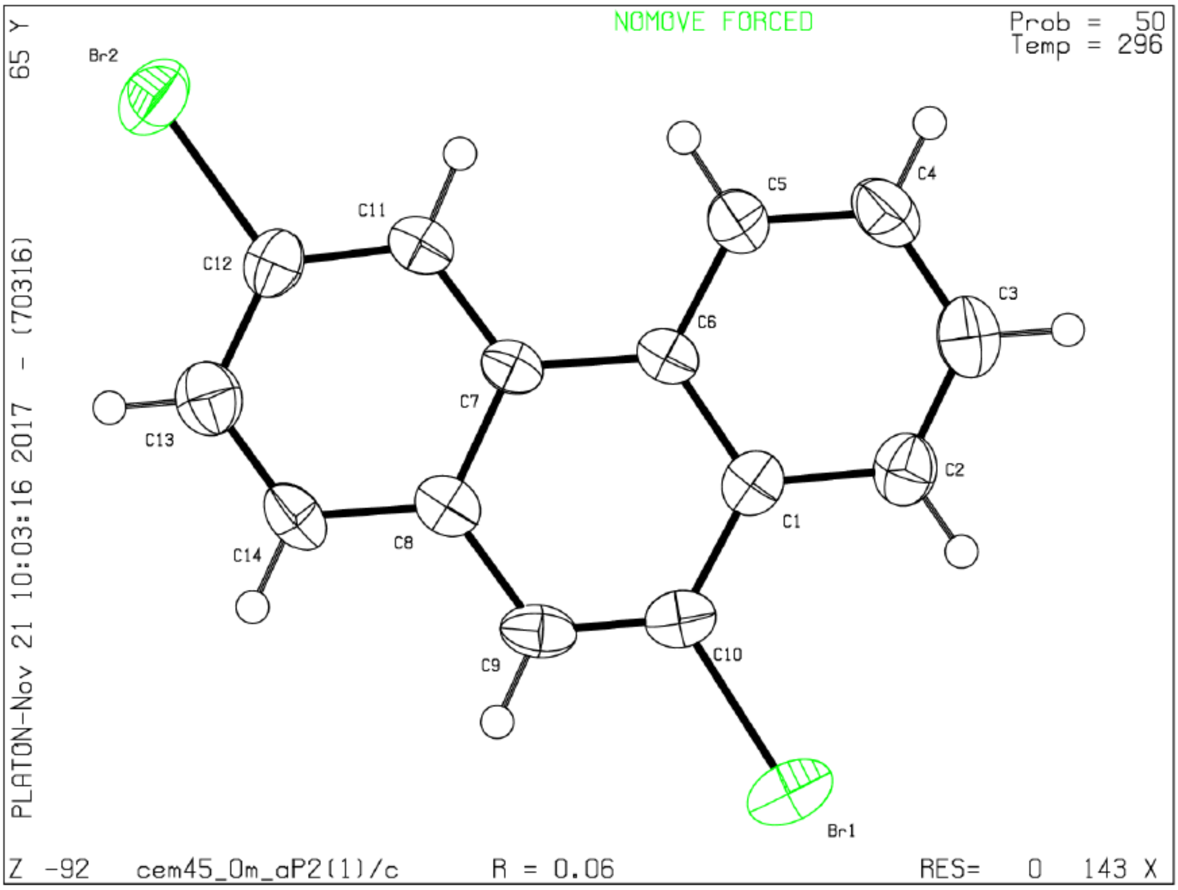
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 09/11/2017; check.def file version of 08/11/2017

Datablock cem45_0m_a - ellipsoid plot



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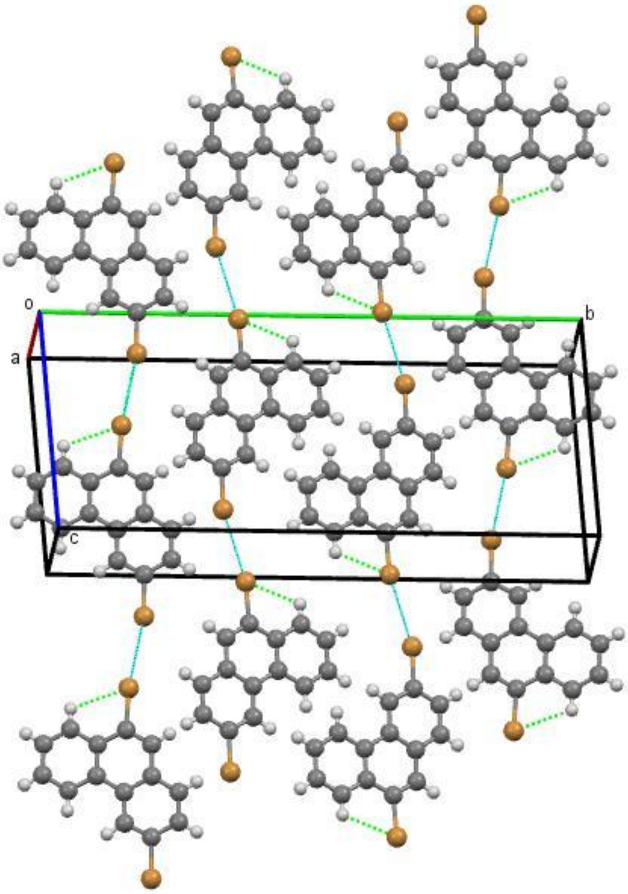
o
a
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