

The Crystal Structure of Solution-Grown 9,10-Diphenylanthracene. A Combined Computational and X-ray Study

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Abstract

The structure of crystals of $C_{26}H_{18}$ (grown from xylene solution) has been solved by the use of relatively simple Buckingham-type atom–atom potential-energy calculations and refined with microdensitometer-scanned film data collected at room temperature. The dihedral angle between the phenyl and anthracene groups is 67° (determined by intermolecular forces) compared with the apparent planarity noted in biphenyl and *p*-terphenyl, and is much closer to the values found for some 1,8-diphenyl-substituted naphthalenes.

Introduction

A structural investigation of 9,10-diphenylanthracene was undertaken primarily to resolve some problems associated with the electron microscopy of this unusually beam-stable compound (Jones, 1976; Parkinson, 1978). It was known that the melt-grown crystals belonged to space group $P2/m$ with $a = 9.99$, $b = 21.06$, $c = 9.11$ Å, $\beta = 112^\circ$, $Z = 4$ (Sloan, 1975). However, crystals used for electron microscopy were grown from xylene and the electron diffraction pattern could not be indexed on the basis of this cell.

It was considered that this structure might prove to be a suitable test for a computational method of structure solution based on the use of atom–atom potentials. Kitaigorodsky & Mirskaya (1972), Kitaigorodsky (1973) and Williams (1969, 1972, 1974) have demonstrated the usefulness of such potentials between non-bonded atoms in the calculation of crystal structures and application of these potentials has been extended to a wide variety of problems in the field of organic solid-state chemistry exemplified by studies of molecular

rearrangements in organic crystals (Gavezzotti & Simonetta, 1975, 1976), rotational disorder (Ramdas & Thomas, 1976) and investigations of extended defects (Ramdas, Thomas & Goringe, 1977). Attempts to improve the basic 6-exp Buckingham potential,*

$$U(r_{ij}) = -A_{\alpha\beta}/r_{ij}^6 + B_{\alpha\beta} \exp(-C_{\alpha\beta} r_{ij}), \quad (1)$$

are being considered (Williams, 1974) in terms of explicit electrostatic interactions to treat the bond moments in addition to including multipolar terms. However, in spite of the need for such developments, (1) still serves as a reliable model potential in describing non-bonded interactions, probably due to the very nature of the derivation of the constants A , B , C from the known experimental data. Notwithstanding its simplicity, the utility of the crystal structure determination with (1) has proved of unique value (Jones, Ramdas & Thomas, 1978), provided that there is prior knowledge of the space group and cell dimensions.

At equilibrium, the first derivatives of the potential energy, which comprises the non-bonded interaction between the atoms of the central molecule with its environment, is zero with respect to the variable parameters (such as Eulerian angles and, in some cases, the translational parameters of molecules from the crystallographic origin and the angles of internal rotation). The basic procedure in the computational solution of the crystal structure involves optimization of the potential energy with respect to these variables, making use of the analytically obtained first and second derivatives. It is the requirement of the optimization procedure for convergence to the equilibrium structure that a prior knowledge of the (very) approximate values of the variables is available. 9,10-Diphenylanthracene is a suitable candidate for such calculations because of the availability of molecular structural data on the two basic skeletons of the molecule, *p*-terphenyl (I, Fig. 1; Rietveld, Maslen & Clews, 1970) and anthracene (II, Fig. 1; Mason, 1964).

* This potential describes the non-bonded interaction between the atoms of type α and β separated by a distance r_{ij} ; the coefficients A , B and C are determined by a fitting procedure to the known experimental data of the crystal structures and heats of sublimation of a number of aromatic hydrocarbons.

Table 1. *Crystal data*

Space group: $C2/c$
 $a = 10.69$ (1), $b = 13.58$ (1), $c = 12.29$ (1) Å
 $(\lambda_{Cu K\alpha} = 1.54178 \text{ Å}) \beta = 90.6$ (2)°
 $d_o = 1.22$; $d_c = 1.23$ Mg m⁻³; $Z = 4$

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Experimental

Colourless, pseudo-hexagonal crystals were obtained from a solution in xylene. Cell parameters were determined from oscillation and Weissenberg photographs and refined by least-squares calculations. The crystal data are given in Table 1. The systematic absences gave the space group as Cc or $C2/c$. The intensities collected from two separate crystals with $Cu K\alpha$ radiation were $h0l-h8l$, which reduced to 856 unique reflexions and $hkh-hk(h-4)$ which were only used for scaling of the b axis data. The films were scanned and the intensities corrected for Lorentz and polarization effects and put on a common scale by the SRC Microdensitometer Service at the Atlas Computer Laboratory. The reliability index predicted for the refinement (comparison of equivalent reflexions) was relatively high. A high non-linearity correction had to be applied to the raw data.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The computations (except for the structure solution itself) were carried out with *SHELX 76*, available on the Manchester CDC 7600.

An $N(z)$ test (Howells, Phillips & Rogers, 1950) showed that the data were consistent with a centrosymmetric structure: the space group $C2/c$ was therefore used throughout the refinement. An $N(z)$ test for a highly symmetric structure often gives a hypercentric distribution and it is possible that the non-centrosymmetric space group should not be excluded. However, it is almost invariably true that a molecule having an inversion centre among its symmetry elements

retains this in the crystal and loses any other symmetry elements. Kitaigorodsky (1973) has shown that with $\bar{1}$ molecular symmetry the closest packed structures are in $P\bar{1}$, $P2_1/c$, $C2/c$ and $Pbca$.

Structure determination

The initial starting point was to make the Cartesian y axis coincident with b because of the similarity of this dimension to that found in p -terphenyl (Rietveld, Maslen & Clews, 1970). In $C2/c$ it is possible that the 9,10-diphenylanthracene molecules might be packed in three different ways within the cell: (i) the molecular centre may coincide with the crystallographic origin (0,0,0), in which case the molecules would be related by a diagonal glide; (ii) the molecule could be on a crystallographic twofold axis $(0, y, \frac{1}{4})$, with molecular centre at $y \sim \frac{1}{4}$; (iii) the molecular centre may be at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and the molecules would be related by a simple c glide. Model (ii) was considered unlikely since it would imply the retention of a twofold axis and the loss of $\bar{1}$ symmetry when the molecule condensed to form the solid. This would be extremely rare (Kitaigorodsky, 1973). Only models (i) and (iii) were considered further.

Molecular packing calculations were carried out with the molecular coordinates generated in terms of 1.4 Å for aromatic C—C, 1.08 Å for C—H and 1.5 Å for C—C distances between the phenyl rings. Bond angles of 120° were assumed for C—C—C and C—C—H. Initially the molecular coordinates were generated for a planar molecule. The long molecular axis was kept parallel to the Cartesian y axis with the short axis in the z direction. Williams's (1974) values for the constants A , B and C were assumed in evaluating the potential energy which included all the interactions ≤ 8 Å; the remainder was evaluated by a convergence approximation (Williams, 1972). Because of the requirement [for both model (i) and model (iii)] that each half of the molecule is related by a centre of inversion, the optimization was carried out with respect to the three Eulerian angles θ_x , θ_y , θ_z and the internal rotation angle φ , the translational parameter remaining invariant. The loss in the conjugation energy upon going from a planar to a non-planar molecular conformation was accounted for by incorporating the following term in the potential-energy expression:

$$E_c = E_c^0 \cos^2 \varphi, \quad (2)$$

where E_c^0 is the conjugation energy of the planar molecule. We assumed a value of E_c^0 of -36 kJ mol^{-1} in conformity with the results of Dewar & Harget (1970) which were obtained from a semi-empirical self-consistent-field molecular orbital treatment of biphenyl; this is also supported by the calculations of Williams (1972) on p, p' -bitolyl.

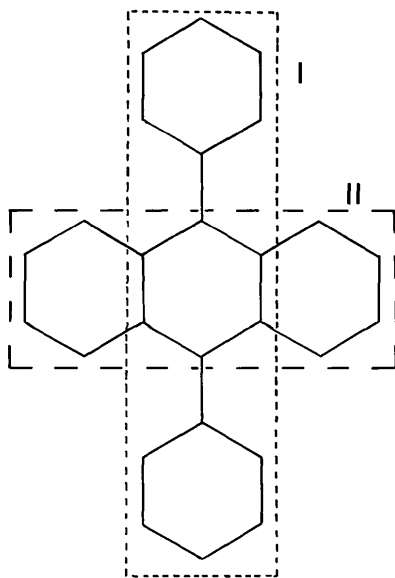


Fig. 1. Molecular skeleton of 9,10-diphenylanthracene split into its component parts: I, p -terphenyl; II, anthracene.

Our calculations for (i) failed to produce convergence to a stable structure. The corresponding optimization in (iii) converged to a structure with a total potential energy of -270 kJ mol^{-1} , of which the intramolecular contribution from non-bonded interactions was 21 kJ mol^{-1} . The conjugation energy was estimated to be $-9.58 \text{ kJ mol}^{-1}$, corresponding to an internal rotation of the phenyl ring by $\sim 70^\circ$ from the plane of the anthracene skeleton. Interatomic short contacts displayed the following features: (i) the shortest non-bonded contacts were between intramolecular atoms, 3.2 \AA for $\text{C}\cdots\text{C}$, 2.56 \AA for $\text{C}\cdots\text{H}$ and 2.2 \AA for $\text{H}\cdots\text{H}$; (ii) all the intermolecular

contacts were within the normal distances expected from their van der Waals radii. This factor, together with the small values for the first derivatives of the potential energy with respect to the variables considered here, strongly indicates a convergence to the structure corresponding to a true minimum in the potential energy.

As a check, the structure was also solved with *MULTAN 76* (Germain, Main & Woolfson, 1971). All unobserved reflexions were given intensities of half the minimum observed value before generating E values. The set of phases with the highest figure of merit gave an E map in which the thirteen largest peaks corresponded to the C atoms determined by the computational approach.

Isotropic refinement reduced R to 0.22, at which point H atoms could be located from a difference synthesis. Again the positions of the H atoms were very close to those given by the computational approach. The refinement of this b axis data (856 reflexions) was continued with anisotropic C atoms and H atoms with fixed isotropic temperature factors. This converged at $R = 0.158$ (154 parameters). Although R was rather high it did not prove possible to locate any significant features on a difference map. It may be noted that in the study of *p*-terphenyl (Rietveld, Maslen & Clews, 1970; Baudour, Delugeard & Cailleau, 1976) difficulties were encountered with high apparent thermal parameters – a feature also of our results, the mean of $(U_{11} + U_{22} + U_{33})$ being 0.082.

The final atomic positions given by the two different approaches are given in Table 2.* Unit weights were used throughout the full-matrix refinement and no correction was made for absorption. The scale factors for the different layers were refined.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34071 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic coordinates*

Those from the computational approach follow the corresponding X-ray refined values.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.8542 (10) 0.868	0.8131 (10) 0.808	0.5206 (8) 0.515
C(2)	0.7413 (10) 0.753	0.8343 (10) 0.837	0.5644 (9) 0.562
C(3)	0.8649 (10) 0.875	0.7224 (10) 0.722	0.4521 (8) 0.453
C(4)	0.7306 (10) 0.746	0.9296 (10) 0.929	0.6344 (9) 0.628
C(5)	0.6557 (11) 0.673	1.0026 (11) 1.008	0.5972 (10) 0.589
C(6)	0.9823 (13) 0.989	0.7058 (11) 0.694	0.4050 (10) 0.406
C(7)	1.0721 (13) 1.091	0.8490 (12) 0.839	0.4894 (13) 0.483
C(8)	1.0845 (12) 1.098	0.7599 (12) 0.752	0.4206 (12) 0.421
C(9)	0.9656 (11) 0.976	0.8692 (11) 0.867	0.5351 (10) 0.530
C(10)	0.6978 (15) 0.733	1.0971 (13) 1.102	0.7581 (13) 0.752
C(11)	0.6420 (12) 0.666	1.0894 (11) 1.095	0.6617 (11) 0.651
C(12)	0.7885 (13) 0.813	0.9338 (11) 0.937	0.7319 (10) 0.728
C(13)	0.7739 (17) 0.806	1.0169 (17) 1.023	0.7966 (12) 0.789
H(1)	0.614 (9) 0.622	1.002 (8) 1.003	0.537 (9) 0.513
H(2)	0.569 (11) 0.610	1.115 (9) 1.156	0.635 (9) 0.622
H(3)	0.681 (10) 0.728	1.153 (9) 1.163	0.820 (9) 0.795
H(4)	0.816 (10) 0.858	1.030 (8) 1.029	0.875 (9) 0.867
H(5)	0.879 (10) 0.870	0.869 (9) 0.876	0.743 (8) 0.758
H(6)	0.972 (11) 0.995	0.665 (10) 0.627	0.359 (10) 0.358
H(7)	1.164 (10) 1.187	0.741 (8) 0.731	0.420 (8) 0.385
H(8)	1.149 (10) 1.175	0.862 (9) 0.884	0.519 (9) 0.494
H(9)	0.965 (10) 0.971	0.897 (9) 0.934	0.606 (9) 0.577

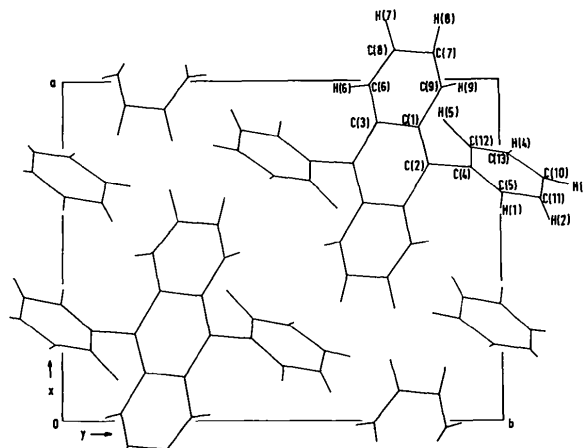


Fig. 2. Projection of the structure along c from $z = 0.25$ to $z = 0.75$. One molecular layer is shown.

Discussion

The basic structures given by the two methods are in close agreement (Table 2). In both, the intermolecular contacts are reasonable. The computational approach, however, assumes standard bond lengths and angles which cannot, therefore, be compared with the X-ray results. The bond distances and angles (X-ray results, Table 3) involving C atoms are all reasonably close to the values found in related structures, although the variation in aromatic C—C distances from 1.30 (2) to 1.48 (2) Å is large. The parameters associated with the

H atoms are satisfactory except for C(12)—H(5) which is long, 1.31 (12) Å. Again in agreement with the computational approach there are no abnormally short intermolecular contacts, the shortest being (C—H) 2.81 Å for C(1) at $x, 2 - y, \frac{1}{2} + z$ to H(4) and (H—H) 2.51 Å for H(9) at $2 - x, y, \frac{1}{2} - z$ to H(5). The molecular packing is shown in Figs. 2 and 3.

A comparison of this structure can be made with those of biphenyl (Trotter, 1961; Robertson, 1961) and *p*-terphenyl (Rietveld, Maslen & Clews, 1970; Baudour, Delugeard & Cailleau, 1976). Biphenyl is found to be completely planar and the distortion necessary to reduce the *ortho* H—H contacts is an in-plane effect [although recent work by Charbonneau & Delugeard (1976, 1977) has suggested that the apparent planarity is statistical in nature]. In *p*-terphenyl at room temperature the molecule is almost planar, the angle between the outer and inner phenyl rings being only 24°. Again in order to reduce the interaction between the *ortho* H atoms of the different phenyl groups there is a distortion of the molecule in the molecular plane. The small degree of twist found here is ascribed to intermolecular forces. In both these cases the *ortho* H—H distances are smaller than those predicted from the accepted van der Waals radii (*i.e.* 2.34 Å) at 2.07 Å (biphenyl) and 2.11 Å (*p*-terphenyl).

In this structure we have evidence of the ease of rotation about the single bond between the phenyl groups and the anthracene fragment. The equations of the least-squares planes are given in Table 4. The angle between the moieties is 67° and must be due to intermolecular forces. It would therefore be predicted that the *ortho* H—H contact distance would be much larger than in biphenyl or *p*-terphenyl, but the poorly defined H(5) makes a close contact H(5)···H(9) of only 1.96 Å whereas the contact H(1)—H(6') is more reasonable. This structure is not unique in having the phenyl groups twisted out of the plane. In 1,3,5-triphenyl-

Table 3. Bond lengths (Å) and angles (°)

Atoms denoted by a prime are generated from the original set by inversion through the centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

C(1)—C(2)	1.36 (1)	C(1)—C(2)—C(3')	123.3 (1.1)
C(1)—C(3)	1.50 (2)	C(1)—C(2)—C(4)	117.7 (1.0)
C(1)—C(9)	1.42 (2)	C(1)—C(3)—C(6)	115.9 (1.1)
C(2)—C(4)	1.56 (2)	C(1)—C(3)—C(2')	117.4 (1.2)
C(2)—C(3')	1.39 (2)	C(2)—C(1)—C(3)	118.0 (1.0)
C(3)—C(6)	1.41 (2)	C(2)—C(1)—C(9)	125.7 (1.2)
C(4)—C(5)	1.35 (2)	C(2)—C(4)—C(5)	118.9 (1.1)
C(4)—C(12)	1.34 (2)	C(2)—C(4)—C(12)	119.4 (1.2)
C(5)—C(11)	1.43 (2)	C(3)—C(1)—C(9)	116.2 (1.1)
C(6)—C(8)	1.33 (2)	C(3)—C(6)—C(8)	126.0 (1.3)
C(7)—C(8)	1.48 (2)	C(4)—C(2)—C(3')	118.7 (1.4)
C(7)—C(9)	1.30 (2)	C(4)—C(5)—C(11)	118.8 (1.2)
C(10)—C(11)	1.33 (2)	C(4)—C(12)—C(13)	119.4 (1.5)
C(10)—C(13)	1.44 (2)	C(5)—C(4)—C(12)	122.5 (1.3)
C(12)—C(13)	1.39 (2)	C(5)—C(11)—C(10)	120.9 (1.4)
C(5)—H(1)	0.86 (11)	C(6)—C(3)—C(2')	124.7 (1.4)
C(11)—H(2)	0.91 (11)	C(6)—C(8)—C(7)	117.1 (1.2)
C(10)—H(3)	1.09 (11)	C(7)—C(9)—C(1)	124.6 (1.3)
C(13)—H(4)	1.07 (11)	C(8)—C(7)—C(9)	120.0 (1.2)
C(12)—H(5)	1.31 (12)	C(10)—C(13)—C(12)	119.6 (1.6)
C(6)—H(6)	0.80 (11)	C(11)—C(10)—C(13)	118.9 (1.5)
C(8)—H(7)	0.89 (11)		
C(7)—H(8)	0.91 (11)		
C(9)—H(9)	0.95 (11)		

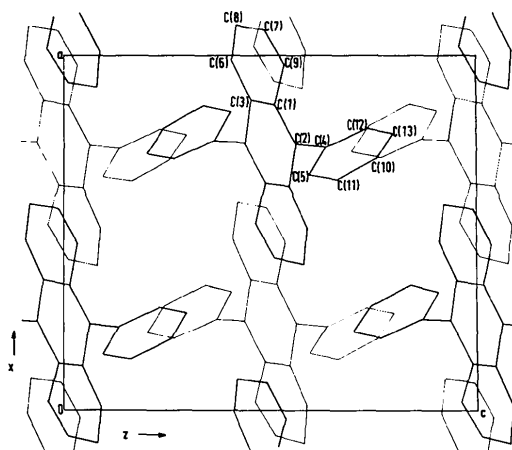


Fig. 3. Projection of the structure down *b*. Molecules centred at $y = \frac{1}{4}$ are shown in bold, those centred at $y = \frac{3}{4}$ in narrow lines.

Table 4. Least-squares planes (direct space) and deviations (Å) of atoms from them

(a) Through the anthracene fragment			
$2.5592x - 7.3923y + 9.8494z = 1.2999$			
C(1)	0.003	C(4)	-0.054
C(2)	-0.011	C(5)	-1.151
C(3)	0.026	C(10)	-0.157
C(6)	-0.015	C(11)	-1.193
C(7)	-0.012	C(12)	1.024
C(8)	-0.001	C(13)	1.010
C(9)	0.016		
(b) Through the phenyl group			
$8.5471x + 5.6406y - 5.4346z = 8.0289$			
C(4)	0.011	C(11)	0.007
C(5)	-0.015	C(12)	0.000
C(10)	0.004	C(13)	-0.008

benzene (Farag, 1954) the rings are twisted by $\sim 30^\circ$ and in hexamethylbenzene (Bart, 1968) the phenyl groups are twisted *ca* 65° from the plane of the central ring. In the low-temperature form of *p*-terphenyl (Baudour, Delugeard & Cailleau, 1976) there is a double minimum in the potential well so that the twist angle can be near 16 or 25° . In the related compounds 1,8-diphenylnaphthalene, *peri*-diphenylacenaphthene and in 1,4,5,8-tetraphenylnaphthalene the torsion angles are found to be 67 , 57 and 58° respectively. The large variation in this parameter stresses the dependence on molecular environment.

After this work was complete our attention was drawn to another determination of the structure of the title compound (Korp, 1975). The essential features of the structure are consistent in the two determinations.

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Static Disorder in a True Racemate: 3-(*o*-Chlorophenylimino)camphor

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Abstract

The phase diagram between the (+) and (±) forms of the title compound, C₁₆H₁₈ClNO, suggests that this system should give solid solutions at all compositions. The structures of the two forms were solved at room temperature. The (±) form is monoclinic, space group

$P2_1/a$, with $Z = 4$, $a = 13.795$ (28), $b = 10.442$ (21), $c = 10.464$ (21) Å, $\beta = 105.08$ (3). The (±) form is a true but disordered racemate. The computation of the intramolecular energy proves the possible existence of three different molecular conformations found in the structure of (+) and (±) forms. R was 7.5% [$I \geq 3\sigma(I)$] and 5.8% [$I \geq 4\sigma(I)$] for the (+) and (±) forms respectively.

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