

The Crystal and Molecular Structure of the *cis*-Dimer of Acenaphthylene

BY T. R. WELBERRY

Department of Chemical Crystallography, University College, Gower Street, London W.C.1, England

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The crystal structure of the *cis*-dimer of acenaphthylene, $C_{24}H_{16}$, has been determined by three-dimensional X-ray analysis ($R=0.070$ for 950 reflexions). The space group is monoclinic $P2_1/c$ with $a=11.966$ (5), $b=13.930$ (5), $c=10.003$ (3) Å $\beta=107.7$ (1), $Z=4$, $D_x=1.24$, $D_m=1.26$ g.cm $^{-3}$. The bond lengths in the naphthalene rings are not significantly different from those in naphthalene itself or acenaphthene. The cyclobutane single bonds of 1.56 Å are greater than a normal single bond. The molecular symmetry deviates from $mm2$ by a small but significant amount. A large ring-bending amplitude of vibration of the cyclobutane ring is indicated by the analysis of thermal parameters. All measurements were at 22°C.

Introduction

Of the two dimers of acenaphthylene, $C_{12}H_8$, that are produced when acenaphthylene is irradiated with ultraviolet light, the *cis*-dimer is the one with the lower melting point (234°C). This stereoisomer was reported by Wei & Livingston (1967) to be the more dominant product, both when oxygen is present in the irradiated solution, and at temperatures above about 60°C in the solid state. The *trans*-dimer (m.p. 304°C) on the other hand is produced at low oxygen concentrations in solution, and at lower temperatures (0–30°C) in the solid state. The present work is part of an investigation into the mechanisms of the reactions occurring in this system. The structure of the *trans*-dimer and the cell dimensions and space group of the *cis*-dimer were reported by Dunitz & Weissman (1949). Both molecules are of interest chemically as they contain four-, five-, and six-membered rings; in particular the cyclobutane ring is of interest. Dunitz's structure furnished strong evidence for a bond length greater than 1.54 Å for the bonds in this ring, but his values taken from an electron density projection had large experimental errors. Although many cyclobutanes do not have a planar ring, his space group contained the molecules in centrosymmetric positions so that the planarity of the ring was assumed.

Experimental

A sample of the *cis*-dimer was produced by the irradiation of a concentrated solution of acenaphthylene in ethanol. This was contained in a Pyrex flask in the presence of air, and unfiltered radiation from a mercury-vapour lamp was used. The product of dimerization was precipitated on formation as a white powder. On separation and subsequent recrystallization from toluene, colourless transparent crystals were obtained. A fairly large prism-shaped crystal (0.5 × 0.5 × 0.9 mm) was chosen with well-defined edges. The prism axis was later found to be [101]. Cell dimen-

sions measured from Straumanis-loaded oscillation photographs taken at 22°C were found to be:

$$a=11.966$$
 (5), $b=13.930$ (5), $c=10.003$ (5) Å;
 $\beta=107.7$ (1)°.

Figures in brackets are the estimated standard deviations on the least significant digits. The measured density at 22°C was 1.26 and the calculated density 1.24 g.cm $^{-3}$ for four molecules per unit cell. Although the values for a, b, c, β agree within about one per cent with the data given by Dunitz, the glide plane in this orientation is c and not n , as given by him. A transformation of axes to give an n -glide cell results in a much larger β angle.

Intensity data were collected from conventional Weissenberg photographs of $h0l$ to $h9l$ with Cu $K\alpha$ radiation. The multiple-film technique was used and as many as seven films were needed to record the range of intensities from a given layer. Intensities were measured using a Joyce-Loebl Flying Spot Microdensitometer. In all about 1150 reflexions were recorded, and only a few were discarded because of their situation on or near white-radiation streaks. Structure amplitudes were computed with the *Intensity Processing Program for the Pegasus Computer* (Milledge & Walley, unpublished). This program scales and averages the data taking into account the errors in intensity measurement, applies Lorentz and polarization corrections, and prints a list of structure factors. The ten different layers were scaled together approximately by measuring common reflexions on a zero-layer photograph with [101] as the rotation axis. These scale factors were later allowed to refine.

Determination of the structure

For the initial stages of structure solution only the 450 strongest low-order reflexions were used. The general packing of the molecules was deduced from a Patterson projection on (010), and trial and error methods were then used to fix the orientation of the molecule.

This proved difficult as the angle between the two halves of the molecule was unknown, and hence a squaring-up technique as described by Milledge (1962) was used on each half separately so that the two planes could be refined to give the best fit. When the R value was about 0.30, individual atomic shifts were allowed and subsequent cycles of x, y, z , and isotropic B refinement produced an R value of 0.096 for 450 reflexions. These stages of the procedure were carried out on the Pegasus computer using the *Diagonal Least Squares* program of Milledge (1962).

Refinement of the structure

Positional and thermal parameters were refined with the complete data using the full-matrix least-squares program [a local modification of Ibers' *NUGLS*, see e.g. Ibers & Bright (1968)] on the University College IBM 360/65 computer. The quantity minimized was $\sum w(F_o - F_c)^2$, w being taken as unity throughout. Atomic scattering factors were those listed in *International Tables for X-ray Crystallography* (1962). An empirical extinction correction was applied to the data.

Table 1. *Parameter list*

Figures in brackets are the estimated standard deviations on the least significant digits. Anisotropic thermal ellipsoids for the carbon atoms took the form

$$\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)].$$

Hydrogen atoms were assumed to have isotropic temperature factors of 2.5 \AA^2 .

ATOM	X-FRAC.	Y-FRAC.	Z-FRAC.	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
C1	0.10607(60)	0.15748(62)	0.31576(71)	0.00764(69)	0.00376(75)	0.00760(92)	-0.00014(50)	0.00189(66)	-0.00232(65)
C2	0.09598(58)	0.07430(61)	0.41474(69)	0.00639(63)	0.00474(79)	0.00763(86)	-0.00008(53)	0.00283(62)	-0.00213(63)
C3	0.23585(62)	0.17954(66)	0.35934(69)	0.00709(68)	0.00123(81)	0.00766(86)	-0.00064(57)	0.00247(64)	-0.00235(62)
C4	0.21533(58)	0.05301(58)	0.50714(67)	0.00683(64)	0.00276(71)	0.00717(83)	-0.00002(53)	0.00374(63)	-0.00055(58)
C5	0.20940(71)	0.24378(70)	0.20990(77)	0.00988(85)	0.00481(85)	0.01103(107)	-0.00043(65)	0.00354(70)	0.00038(72)
C6	0.25988(67)	-0.01492(65)	0.60916(72)	0.00630(64)	0.00441(81)	0.00851(95)	0.00069(61)	0.00301(77)	0.00019(68)
C7	0.42411(73)	0.74543(76)	0.37600(80)	0.01009(90)	0.00160(100)	0.01531(122)	0.00071(71)	0.00158(90)	-0.00130(87)
C8	0.38514(74)	-0.01007(72)	0.67698(69)	0.01028(87)	0.00697(92)	0.00068(89)	0.00168(71)	0.00159(73)	0.00044(70)
C9	0.42400(66)	0.18439(72)	0.48589(88)	0.00723(78)	0.00709(100)	0.01451(120)	-0.00048(66)	0.00401(83)	-0.00395(84)
C10	0.43850(63)	0.04693(67)	0.64135(74)	0.00736(70)	0.00326(80)	0.00078(91)	0.00172(61)	0.00143(67)	-0.00007(67)
C11	0.29221(54)	0.11530(59)	0.66311(63)	0.00538(60)	0.00346(69)	0.00633(80)	0.00018(54)	0.00246(57)	-0.00089(58)
C12	0.41599(57)	0.11399(63)	0.53388(66)	0.00595(62)	0.00373(73)	0.00030(90)	-0.00019(58)	0.00153(56)	-0.00114(62)
C13	0.05555(57)	0.09084(62)	0.18724(68)	0.00516(60)	0.00327(78)	0.00051(87)	0.00091(56)	0.00051(58)	-0.00027(66)
C14	0.05649(55)	0.00346(61)	0.28374(66)	0.00328(61)	0.00355(80)	0.00044(91)	-0.00164(54)	0.00064(60)	-0.00149(63)
C15	0.14074(52)	0.04691(60)	0.11718(63)	0.00669(67)	0.00162(72)	0.00542(74)	0.00144(57)	0.00052(56)	-0.00022(59)
C16	0.10634(58)	-0.07955(60)	0.26163(70)	0.00616(64)	0.00283(78)	0.00083(80)	-0.00115(54)	0.00119(61)	-0.00072(61)
C17	0.12465(73)	0.08401(64)	0.02700(71)	0.01280(95)	0.00353(75)	0.00886(92)	0.00053(67)	0.00350(77)	0.00007(64)
C18	0.12093(62)	-0.16703(63)	0.31372(73)	0.00647(75)	0.00136(80)	0.00091(100)	-0.00147(62)	0.00226(71)	0.00017(67)
C19	0.27224(76)	0.03431(77)	-0.01420(80)	0.01021(87)	0.00489(92)	0.00721(90)	-0.00113(72)	0.00263(77)	-0.00197(71)
C20	0.29483(79)	-0.23965(68)	0.26872(80)	0.01119(90)	0.00197(82)	0.01271(112)	-0.00012(77)	0.00136(84)	-0.00081(74)
C21	0.25955(64)	-0.06915(68)	0.02517(71)	0.00760(72)	0.00520(91)	0.00060(90)	-0.00031(62)	0.00369(67)	-0.00163(67)
C22	0.25210(65)	-0.20344(66)	0.17459(78)	0.00805(75)	0.00279(83)	0.01144(106)	0.00003(60)	0.00251(72)	-0.00063(72)
C23	0.16431(53)	-0.04624(57)	0.16349(62)	0.00448(57)	0.00269(72)	0.00384(77)	0.00018(50)	0.00003(54)	-0.00126(56)
C24	0.23931(53)	-0.11021(63)	0.12093(64)	0.00533(61)	0.00222(76)	0.00770(89)	0.00004(53)	0.00034(62)	-0.00191(59)

ATOM	X-FRAC.	Y-FRAC.	Z-FRAC.	ATOM	X-FRAC.	Y-FRAC.	Z-FRAC.
H1	0.06419	0.21422	0.34057	H9	-0.01816	0.10659	0.11548
H2	0.04554	0.09700	0.47555	H10	0.05373	-0.00779	0.24506
H3	0.26222	0.29100	0.23488	H11	0.18138	0.15363	-0.00718
H4	0.20546	-0.06046	0.63855	H12	0.07430	-0.18853	0.38127
H5	0.47311	0.29316	0.34449	H13	0.31354	0.04859	-0.08657
H6	0.42819	-0.06150	0.75436	H14	0.20020	-0.29890	0.30383
H7	0.57953	0.28008	0.52834	H15	0.35049	-0.11356	-0.00803
H8	0.54567	0.04558	0.68900	H16	0.30840	-0.24970	0.14590

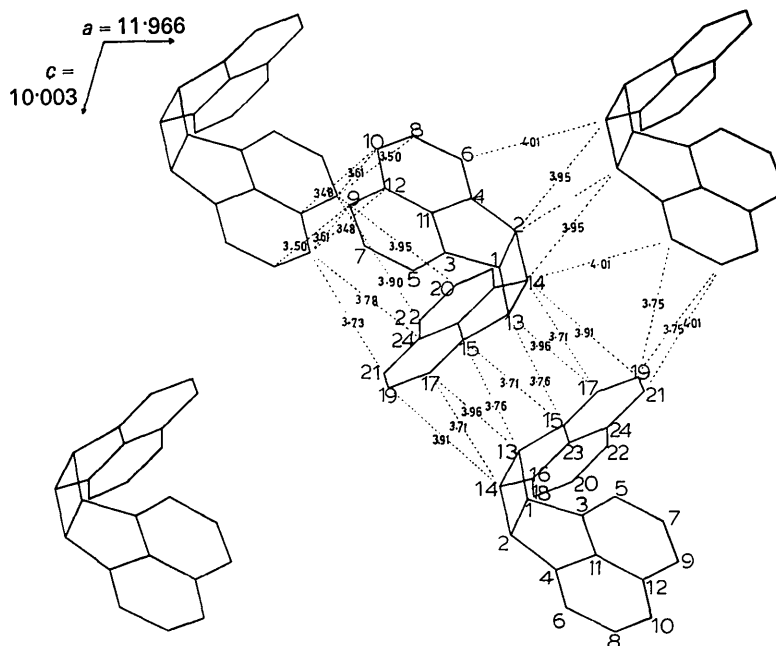


Fig. 1. Molecular packing. Molecules related by a c -glide are omitted. Distances given are in Ångströms.

This took the form of a parameter b in the equation $I_{\text{true}} = I_{\text{obs}} + b \cdot I_{\text{obs}}^2$. With I on an absolute scale a value of 7×10^{-6} for b was found to give satisfactory improvement in many of the strong low-order reflexions. A few remaining

Table 2. Structure factor list.

Observed and calculated structure factors in electrons. $F(000) = 640$ electrons.

H	K	L	F(o)	F(c)	H	K	L	F(o)	F(c)	H	K	L	F(o)	F(c)	H	K	L	F(o)	F(c)	H	K	L	F(o)	F(c)	H	K	L	F(o)	F(c)
1	0	0	640	640	1	0	0	640	640	1	0	0	640	640	1	0	0	640	640	1	0	0	640	640	1	0	0	640	640
1	0	0	320	320	1	0	0	320	320	1	0	0	320	320	1	0	0	320	320	1	0	0	320	320	1	0	0	320	320
1	0	0	160	160	1	0	0	160	160	1	0	0	160	160	1	0	0	160	160	1	0	0	160	160	1	0	0	160	160
1	0	0	80	80	1	0	0	80	80	1	0	0	80	80	1	0	0	80	80	1	0	0	80	80	1	0	0	80	80
1	0	0	40	40	1	0	0	40	40	1	0	0	40	40	1	0	0	40	40	1	0	0	40	40	1	0	0	40	40
1	0	0	20	20	1	0	0	20	20	1	0	0	20	20	1	0	0	20	20	1	0	0	20	20	1	0	0	20	20
1	0	0	10	10	1	0	0	10	10	1	0	0	10	10	1	0	0	10	10	1	0	0	10	10	1	0	0	10	10
1	0	0	5	5	1	0	0	5	5	1	0	0	5	5	1	0	0	5	5	1	0	0	5	5	1	0	0	5	5
1	0	0	2.5	2.5	1	0	0	2.5	2.5	1	0	0	2.5	2.5	1	0	0	2.5	2.5	1	0	0	2.5	2.5	1	0	0	2.5	2.5
1	0	0	1.25	1.25	1	0	0	1.25	1.25	1	0	0	1.25	1.25	1	0	0	1.25	1.25	1	0	0	1.25	1.25	1	0	0	1.25	1.25
1	0	0	0.625	0.625	1	0	0	0.625	0.625	1	0	0	0.625	0.625	1	0	0	0.625	0.625	1	0	0	0.625	0.625	1	0	0	0.625	0.625
1	0	0	0.3125	0.3125	1	0	0	0.3125	0.3125	1	0	0	0.3125	0.3125	1	0	0	0.3125	0.3125	1	0	0	0.3125	0.3125	1	0	0	0.3125	0.3125
1	0	0	0.15625	0.15625	1	0	0	0.15625	0.15625	1	0	0	0.15625	0.15625	1	0	0	0.15625	0.15625	1	0	0	0.15625	0.15625	1	0	0	0.15625	0.15625
1	0	0	0.078125	0.078125	1	0	0	0.078125	0.078125	1	0	0	0.078125	0.078125	1	0	0	0.078125	0.078125	1	0	0	0.078125	0.078125	1	0	0	0.078125	0.078125
1	0	0	0.0390625	0.0390625	1	0	0	0.0390625	0.0390625	1	0	0	0.0390625	0.0390625	1	0	0	0.0390625	0.0390625	1	0	0	0.0390625	0.0390625	1	0	0	0.0390625	0.0390625
1	0	0	0.01953125	0.01953125	1	0	0	0.01953125	0.01953125	1	0	0	0.01953125	0.01953125	1	0	0	0.01953125	0.01953125	1	0	0	0.01953125	0.01953125	1	0	0	0.01953125	0.01953125
1	0	0	0.009765625	0.009765625	1	0	0	0.009765625	0.009765625	1	0	0	0.009765625	0.009765625	1	0	0	0.009765625	0.009765625	1	0	0	0.009765625	0.009765625	1	0	0	0.009765625	0.009765625
1	0	0	0.0048828125	0.0048828125	1	0	0	0.0048828125	0.0048828125	1	0	0	0.0048828125	0.0048828125	1	0	0	0.0048828125	0.0048828125	1	0	0	0.0048828125	0.0048828125	1	0	0	0.0048828125	0.0048828125
1	0	0	0.00244140625	0.00244140625	1	0	0	0.00244140625	0.00244140625	1	0	0	0.00244140625	0.00244140625	1	0	0	0.00244140625	0.00244140625	1	0	0	0.00244140625	0.00244140625	1	0	0	0.00244140625	0.00244140625
1	0	0	0.001220703125	0.001220703125	1	0	0	0.001220703125	0.001220703125	1	0	0	0.001220703125	0.001220703125	1	0	0	0.001220703125	0.001220703125	1	0	0	0.001220703125	0.001220703125	1	0	0	0.001220703125	0.001220703125
1	0	0	0.0006103515625	0.0006103515625	1	0	0	0.0006103515625	0.0006103515625	1	0	0	0.0006103515625	0.0006103515625	1	0	0	0.0006103515625	0.0006103515625	1	0	0	0.0006103515625	0.0006103515625	1	0	0	0.0006103515625	0.0006103515625
1	0	0	0.00030517578125	0.00030517578125	1	0	0	0.00030517578125	0.00030517578125	1	0	0	0.00030517578125	0.00030517578125	1	0	0	0.00030517578125	0.00030517578125	1	0	0	0.00030517578125	0.00030517578125	1	0	0	0.00030517578125	0.00030517578125
1	0	0	0.000152587890625	0.000152587890625	1	0	0	0.000152587890625	0.000152587890625	1	0	0	0.000152587890625	0.000152587890625	1	0	0	0.000152587890625	0.000152587890625	1	0	0	0.000152587890625	0.000152587890625	1	0	0	0.000152587890625	0.000152587890625
1	0	0	7.62e-05	7.62e-05	1	0	0	7.62e-05	7.62e-05	1	0	0	7.62e-05	7.62e-05	1	0	0	7.62e-05	7.62e-05	1	0	0	7.62e-05	7.62e-05	1	0	0	7.62e-05	7.62e-05
1	0	0	3.81e-05	3.81e-05	1	0	0	3.81e-05	3.81e-05	1	0	0	3.81e-05	3.81e-05	1	0	0	3.81e-05	3.81e-05	1	0	0	3.81e-05	3.81e-05	1	0	0	3.81e-05	3.81e-05
1	0	0	1.905e-05	1.905e-05	1	0	0	1.905e-05	1.905e-05	1	0	0	1.905e-05	1.905e-05	1	0	0	1.905e-05	1.905e-05	1	0	0	1.905e-05	1.905e-05	1	0	0	1.905e-05	1.905e-05
1	0	0	9.525e-06	9.525e-06	1	0	0	9.525e-06	9.525e-06	1	0	0	9.525e-06	9.525e-06	1	0	0	9.525e-06	9.525e-06	1	0	0	9.525e-06	9.525e-06	1	0	0	9.525e-06	9.525e-06
1	0	0	4.7625e-06	4.7625e-06	1	0	0	4.7625e-06	4.7625e-06	1	0	0	4.7625e-06	4.7625e-06	1	0	0	4.7625e-06	4.7625e-06	1	0	0	4.7625e-06	4.7625e-06	1	0	0	4.7625e-06	4.7625e-06
1	0	0	2.38125e-06	2.38125e-06	1	0	0	2.38125e-06	2.38125e-06	1	0	0	2.38125e-06	2.38125e-06	1	0	0	2.38125e-06	2.38125e-06	1	0	0	2.38125e-06	2.38125e-06	1	0	0	2.38125e-06	2.38125e-06
1	0	0	1.190625e-06	1.190625e-06	1	0	0	1.190625e-06	1.190625e-06	1	0	0	1.190625e-06	1.190625e-06	1	0	0	1.190625e-06	1.190625e-06	1	0	0	1.190625e-06	1.190625e-06	1	0	0	1.190625e-06	1.190625e-06
1	0	0	5.953125e-07	5.953125e-07	1	0	0	5.953125e-07	5.953125e-07	1	0	0	5.953125e-07	5.953125e-07	1	0	0	5.953125e-07	5.953125e-07	1	0	0	5.953125e-07	5.953125e-07	1	0	0	5.953125e-07	5.953125e-07
1	0	0	2.9765625e-07	2.9765625e-07	1	0	0	2.9765625e-07	2.9765625e-07	1	0	0	2.9765625e-07	2.9765625e-07	1	0	0	2.9765625e-07	2.9765625e-07	1	0	0	2.9765625e-07	2.9765625e-07	1	0	0	2.9765625e-07	2.9765625e-07
1	0	0	1.48828125e-07	1.48828125e-07	1	0	0	1.48828125e-07	1.48828125e-07	1	0	0	1.48828125e-07	1.48828125e-07	1	0	0	1.48828125e-07	1.48828125e-07	1	0	0	1.48828125e-07	1.48828125e-07	1	0	0	1.48828125e-07	1.48828125e-07
1	0	0	7.44140625e-08	7.44140625e-08	1	0	0	7.44140625e-08	7.44140625e-08	1	0	0	7.44140625e-08	7.44140625e-08	1	0	0	7.44140625e-08	7.44140625e-08	1	0	0	7.44140625e-08	7.44140625e-08	1	0	0	7.44140625e-08	7.44140625e-08
1	0	0	3.720703125e-08	3.720703125e-08	1	0	0	3.720703125e-08	3.720703125e-08	1	0	0	3.720703125e-08	3.720703125e-08	1	0	0	3.720703125e-08	3.720703125e-08	1	0	0	3.720703125e-08	3.720703125e-08	1	0	0	3.720703125e-08	3.720703125e-08
1	0	0	1.8603515625e-08	1.8603515625e-08	1	0	0	1.8603515625e-08	1.8603515625e-08	1	0	0	1.8603515625e-08	1.8603515625e-08	1	0	0	1.8603515625e-08	1.8603515625e-08	1	0	0	1.8603515625e-08	1.8603515625e-08	1	0	0	1.8603515625e-08	1.8603515625e-08
1	0	0	9.3017578125e-09	9.3017578125e-09	1	0	0	9.3017578125e-09	9.3017578125e-09	1	0	0	9.3017578125e-09	9.3017578125e-09	1	0	0	9.3017578125e-09	9.3017578125e-09	1	0	0	9.3017578125e-09	9.3017578125e-09	1	0	0	9.3017578125e-09	9.3017578125e-09
1	0	0	4.65087890625e-09	4.65087890625e-09	1	0	0	4.65087890625e-09	4.65087890625e-09	1	0	0	4.65087890625e-09	4.65087890625e-09	1	0	0	4.65087890625e-09	4.65087890625e-09	1	0	0	4.65087890625e-09	4.65087890625e-09	1	0	0	4.65087890625e-09	4.65087890625e-09
1	0	0	2.325439453125e-09	2.325439453125e-09	1	0	0	2.325439453125e-09	2.325439453125e-09	1	0	0	2.325439453125e-09	2.325439453125e-09	1	0	0	2.325439453125e-09	2.325439453125e-09	1	0	0	2.325439453125e-09	2.325439453125e-09	1	0	0	2.325439453125e-09	2.325439453125e-09
1	0	0	1.1627197265625e-09	1.1627197265625e-09	1	0	0	1.1627197265625e-09	1.1627197265625e-09	1	0	0	1.1627197265625e-09	1.1627197265625e-09	1	0	0	1.1627197265625e-09	1.1627197265625e-09	1	0	0	1.1627197265625e-09	1.1627197265625e-09	1	0	0	1.1627197265625e-09	1.1627197265625e-09
1	0	0	5.8135986328125e-10	5.8135986328125e-10	1	0	0	5.8135986328125e-10	5.8135986328125e-10	1	0	0	5.8135986328125e-10	5.8135986328125e-10	1	0	0	5.8135986328125e-10</											

reflexions for which F_{calc} was still much greater than F_{obs} were ones for which measurement had been inaccurate because of insufficient films used in the film-packs. These were omitted from the refinement and are labelled with an X in the structure factors list. A total of 226 parameters were refined using 1144 reflexions, but because of the high number of parameters the refinement was split into two: 72 positional and 10 layer scale, and 144 anisotropic thermal parameters, which were refined alternately. Three cycles were sufficient to reach a minimum of $R=0.080$. At this stage it was noticed that bad agreement of the very weak reflexions was contributing quite a lot of noise to the

refinement. A cycle was therefore performed omitting the reflexions which are marked with an asterisk in the structure factor list. An R value of 0.070 for 950 reflexions resulted, which became 0.076 for 1144 reflexions. The small shifts produced were not considered significant enough to warrant further refinement. Positional parameters and isotropic thermal parameters for hydrogen were assumed but were not refined. A final parameters list is given in Table 1, and observed and calculated structure factors are listed in Table 2. The e.s.d.'s given, which come from the last least-squares cycle, are calculated on the basis of the number of parameters used in each cycle (82 for x, y, z and 144

Table 3. Bond lengths and angles

Estimated standard deviations vary between 0.010 and 0.013 Å for bond lengths and 0.4 and 0.7° for the angles. Numbering of atoms is as shown in Fig. 2.

Bond	Length	Mean	Naphthalene	Acenaphthene
1-2	1.567 Å			
13-14	1.562	1.563	—	—
1-13	1.551			
2-14	1.571			
1-3	1.519			
2-4	1.512	1.520	—	—
13-15	1.527			
14-16	1.520			
3-5	1.356			
4-6	1.375	1.358	1.36	1.37
15-17	1.365			
16-18	1.337			
5-7	1.437			
6-8	1.445	1.433	1.42	1.43
17-19	1.433			
18-20	1.417			
7-9	1.397			
8-10	1.364	1.380	1.36	1.35
19-21	1.365			
20-22	1.392			
9-12	1.422			
10-12	1.418	1.419	1.42	1.42
21-24	1.447			
22-24	1.390			
3-11	1.411			
4-11	1.406	1.409	1.42	1.41
15-23	1.388			
16-23	1.431			
11-12	1.415	1.415	1.41	1.40
23-24	1.415			

Atoms	Angle	Atoms	Angle	Atoms	Angle
1-2-13	90.5°	1-2-3	105.5°	1-3-11	107.3°
1-2-14	90.3	1-2-4	105.0	2-4-11	108.1
1-13-14	91.2	13-15-14	103.4	13-15-23	108.8
2-13-14	91.0	13-16-14	107.6	14-16-23	105.3
3-5-11	121.0	3-5-7	117.2	5-7-9	123.6
4-6-11	119.4	4-6-8	118.0	6-8-10	121.9
15-17-23	119.7	15-17-19	117.4	17-19-21	123.8
16-18-23	121.0	16-18-20	118.4	18-20-22	122.5
7-9-12	118.4	9-12-11	117.5	3-11-12	122.4
8-10-12	121.3	10-12-11	115.8	4-11-12	123.5
19-21-24	119.3	21-24-23	114.8	15-23-24	124.8
20-22-24	119.3	22-24-23	118.6	16-23-24	120.2

for b_{ij}) so that these are slightly smaller than the agreement for the total number of parameters would suggest. Standard deviations for bond lengths were calculated using the formulae of Ahmed & Cruickshank (1953), and those of bond angles using the formula of Darlow (1960).

Discussion

The molecular packing is shown in Fig. 1. A layer related to the one shown by a *c*-glide occurs halfway up the *b* axis. Molecules are packed in rows along a line of centres of symmetry along [101]. Some intermolecular carbon-carbon contact distances are shown. Table 3 lists the bond lengths and bond angles of the derived molecular structure. The bonds in the four-membered ring are greater than the normal single-bond length. Mean values of chemically similar bond lengths are compared with the corresponding bond lengths in naphthalene and acenaphthene (Ehrlich, 1957). The deviation of each bond length from the mean value for that type of bond is never more than 2.5 standard deviations and is generally much less.

The significant findings of the investigation are concerned with the conformation of the molecule. Fig. 2 shows the molecule projected onto the plane of one half of the molecule. The two halves are seen to be twisted with respect to each other, *i.e.* the molecule does not have *mm*2 symmetry. The deviation from this symmetry was measured in terms of the angles between pairs of similar vectors – with the notation as in Figs. 1 and 2:

2-1	14-13	2°	6'
4-3	16-15	3	36
6-5	18-17	4	36
8-7	20-19	5	24
10-9	22-21	5	6

Table 4. Values of $(U_{ij\text{obs}} - U_{ij\text{calc}}) \times 10^4 \text{ \AA}^2$ for rigid-body motion of one half molecule only (atoms 1-12), where $U_{ij} = B_{ij}/8\pi^2$

U_{ij} are referred to molecular axes, L perpendicular to the plane of the half molecule, M parallel to the 11-12 bond, and N forming the orthogonal set

(a) With the centre of rotation at the centre of gravity of the half molecule, (b) with the centre of rotation moved 1 Å towards the 4-membered ring.

The mean standard deviation of the values for U_{ij} was 50 (on this scale), and errors within this range have been omitted.

(a)	11	22	33	23	13	12	(b)	11	22	33	23	13	12
1	-53	+53	-145	+58	—	—	—	—	—	+65	—	—	—
2	-98	—	-141	-72	—	—	—	—	—	+78	—	—	—
3	-87	—	—	+65	-53	—	-54	—	—	+82	—	—	—
4	-65	—	-141	-64	-50	—	—	—	—	-63	—	—	—
5	—	—	—	—	—	—	—	—	—	—	-85	—	—
6	-97	—	-60	—	—	—	—	—	—	—	+72	—	—
7	+77	—	+194	+118	+72	—	—	+54	+87	—	—	+73	—
8	—	—	+99	-109	+121	—	—	—	—	—	—	+109	—
9	+91	—	+267	+95	—	—	—	—	—	+111	+59	—	—
10	+118	—	—	-58	—	-62	—	—	—	-176	—	—	—
11	—	—	-56	—	—	—	—	—	—	-54	—	—	—
12	-83	—	—	—	-55	—	—	—	—	-141	—	-63	—

Derived rigid-body T, ω tensors were:

T_{ij} for	(a)	+0.0224	+0.0402	+0.0418	+0.0025	+0.0027	+0.0025	Å
	(b)	+0.0175	+0.0413	+0.0387	+0.0025	+0.0015	+0.0031	
ω_{ij} for	(a)	+0.0046	+0.0050	+0.0009	+0.0010	-0.0000	-0.0002	radians
	(b)	+0.0041	+0.0048	+0.0023	+0.0007	-0.0004	+0.0001	

This twist can be explained in terms of the non-planar conformation of the cyclobutane ring. While deviations from planarity of the ring itself are only of the order of one standard deviation and hence not significant,

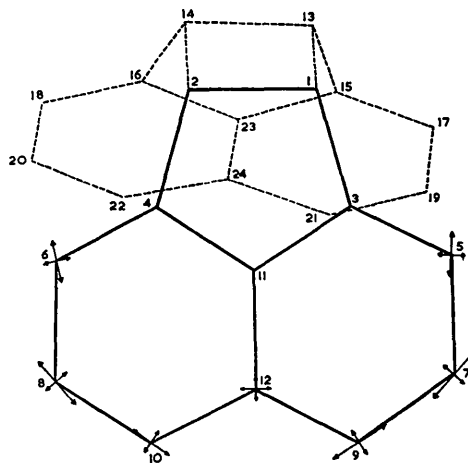


Fig. 2. Molecular conformation and thermal motion. The molecule is projected onto the plane of atoms 1-12. Arrows indicate the directions of maximum and minimum vibration in the plane. These, together with the out-of-plane amplitude, are:

	Maximum	Minimum	Perpendicular
5	5.2	3.5	4.1
6	5.0	3.2	3.0
7	7.6	3.2	5.1
8	6.5	3.2	3.9
9	7.5	3.2	3.7
10	5.3	2.9	3.7
12	3.6	3.1	2.5

Values of $B = 8\pi^2 \bar{u}^2$ in \AA^2 . \bar{u}^2 is the mean-square atomic displacement.

the resulting shifts of the atoms furthest from the cyclobutane are about 20–30 standard deviations and hence highly significant.

Some results of an analysis of the thermal-vibration ellipsoids are also indicated in Fig. 2. The directions of maximum and minimum amplitude of vibration in the plane of one half-molecule are shown. The diagram suggests that the half-molecule pivots about the four-membered ring in a swinging motion in its own plane. Rigid-body T_{ij} , ω_{ij} analyses, after the manner of Cruickshank (1956), were performed on the two halves of the molecule separately. The half-molecule atoms 1–12 gave generally good agreement with the rigid-body model when the centre of rotation was shifted to a point much nearer the four-membered ring than the centre of gravity. Table 4 lists values of $U_{ij\text{obs}} - U_{ij\text{calc}}$ for these atoms. 76% of the U_{ij} lie within one standard deviation for the case of the shifted centre of rotation compared with only 55% for the case where the centre of gravity is the centre of rotation. A large negative difference value is not compatible with any rigid-body model, so that the large difference for U_{33} of atom 10 illustrates that the proposed model for the vibrations is an over-simplification. This difference, however, is in agreement with a general trend that atoms 5, 7, 9 have larger thermal vibrations than atoms 6, 8, 10 respectively. It is perhaps significant that because of the twisted conformation of the molecule as a whole, atoms 5, 7, 9 are respectively further from the centre of gravity of the whole molecule than are atoms 6, 8, 10.

The motion of the other half of the molecule, atoms 13–24, though following the same trends as to which atoms have the large thermal motions, is not so satisfactorily represented by the simple rigid-body model, and seems restricted in directions parallel to **b**. This restricted vibration is not unreasonable in terms of the molecular packing, but it must be borne in mind that several of these atoms have abnormally low thermal vibrations parallel to **b**, and that some bias in the results is possible because of the refinement of layer scale factors normal to **b** as well as b_{ij} values.

However, since the first half of the molecule, atoms 1–12, does not show any sign of such correlation, it is possible that the effect is real and the two unusually low B values of 1.0 and 0.8 Å² of atoms 16 and 18 are due to random errors of the order of two standard deviations.

As the standard deviation for the principal B values is about 0.5 Å², some quite large discrepancies are to be expected. Nevertheless, it is evident that some sort of large vibration exists and within the limits of experiment this can be explained in terms of a twisting motion due to the bending of the cyclobutane ring.

Further investigations are in progress, which are aimed at discovering whether the observed deformation destroying $mm2$ symmetry is a result of inter- rather than intra-molecular forces. Calculations of repulsive intermolecular interactions as a function of amount of twist, in a manner analogous to the methods of Craig, Mason, Pauling & Santry (1965), are being made, together with measurements of thermal-expansion coefficients, and these will form the subject of a separate paper.

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