# Crystal and Molecular Structure of *trans,trans*-Tetrabenzo[*a,c,g,i*]cyclododecene

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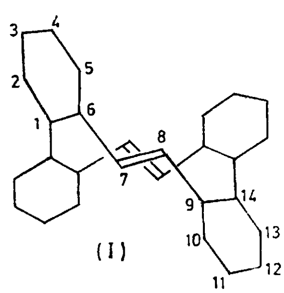
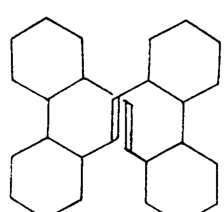
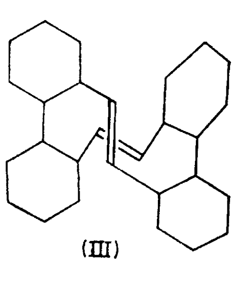
The title compound crystallizes in space group *C*2/*c* with $a$ = 16·810(5), $b$ = 16·694(5), $c$ = 13·835(4) Å, β = 98·41(2)°. The structure was solved by direct methods from diffractometer data and was refined to *R* 0·060 for 2416 independent, observed reflexions. The structure consists of two independent molecules lying in different orientations on crystallographic two-fold axes. This implies that the free molecule has $D_2$ (222) symmetry. The molecular geometry in the crystal structure is discussed in terms of distortion from this symmetry.

THE *trans,trans*-configuration was assigned to one of the tetrabenzo[*a,c,g,i*]cyclododecene isomers reported by Wittig[1] in 1955. This isomer was later shown[2] to be in the *cis,trans*-configuration. Recently, several synthetic routes have been claimed to give genuine *trans,trans*-isomers.[3,4] In order to verify this assignment, and to determine which of the three theoretically possible arrangements of the *trans*-double bonds [(I)—(III)] was present, a complete *X*-ray analysis was undertaken on a specimen of one of the products.[4]



(I)


(II)


(III)

EXPERIMENTAL

*Crystal Data*.—$C_{28}H_{20}$, $M$ = 356. Monoclinic, $a$ = 16·810(5), $b$ = 16·694(5), $c$ = 13·835(4) Å, β = 98·41(2)°, $U$ = 3840·6(8) Å$^3$, $Z$ = 8, $D_c$ = 1·23 g cm$^{-3}$, $F(000)$ = 1504. λ(Cu-$K_\alpha$) = 1·5418 Å, μ(Cu-$K_\alpha$) = 0·5 cm$^{-1}$. Space group *Cc* ($C^4_s$, No. 9) or *C*2/*c* ($C^6_{2h}$, No. 15) from systematic absences, refinement successful in the latter.

Unit-cell and space-group data were obtained by photographic methods. Cell parameters were refined by least-

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1 G. Wittig, G. Koenig, and K. Clausz, *Annalen*, 1955, **593**, 127.
2 H. Irngartinger, *Chem. Ber.*, 1972, **105**, 2068.
3 K. Grohmann, P. D. Howes, R. H. Mitchell, A. Monahan, and F. Sondheimer, *J. Org. Chem.*, 1973, **38**, 808.
4 I. Agranat, M. A. Kraus, E. D. Bergmann, P. J. Roberts, and O. Kennard, *Tetrahedron Letters*, 1973, 1265.

squares treatment of θ values for 27 reflexions on an automatic Picker diffractometer by use of Cu-$K_\alpha$ radiation reflected from a graphite monochromator. Intensities were measured for a crystal of length 0·40 and cross-section 0·14 × 0·22 mm. The diffractometer was operated in the θ—2θ scan mode with a range in 2θ in (2·0 + 0·2601 tan θ)° and at a speed of 1° min$^{-1}$. The standard deviation of an intensity was calculated from counting statistics according to $\sigma^2 (I) = S + B + (dS)^2$ where $S$ = scan count, $B$ = background corrected to scan time, $I = S - B$, and $d$ is a constant which allows for instrumental instability, calculated as 0·04 from monitor reflexions. Of 3282 independent reflexions with 2θ(Cu-$K_\alpha$) ⩽ 127° (minimum interplanar spacing 0·86 Å), 866 were classified as unobserved, having $I/\sigma(I) < 3{\cdot}0$ and were eliminated from subsequent calculations. No absorption correction was made. Lorentz and polarization factors were applied and the structure amplitudes and normalized structure amplitudes ($E$ values) were derived. An examination of the $E$ statistics (Table 1)

TABLE 1

Distribution (%) of reflexions in ranges of $|E|$ and overall average $|E^2 - 1|$ for (a) this structure, and theoretical values for (b) centrosymmetric, and (c) non-centrosymmetric cases

| | 0·0—0·2 | 0·3—0·8 | 0·8—2·0 | $<\|E^2 - 1\|>$ |
|---|---|---|---|---|
| (a) | 38·4 | 20·9 | 18·8 | 1·058 |
| (b) | 34·5 | 21·3 | 21·4 | 0·968 |
| (c) | 18·1 | 29·2 | 31·4 | 0·736 |

showed that the structure was centrosymmetric and in all subsequent work we used the space group $C2/c$.

The structure was solved by weighted tangent-formula refinement [5] applied to 596 reflexions with $|E| \geqslant 1{\cdot}25$. The iteration was begun with nine reflexions (Table 2). The

TABLE 2

Reflexions used in starting set with allowed phases (rad)

| | | | |
|---|---|---|---|
| 2 | 2 | 3 | 0 |
| 3 | 1 | 1 | 0 |
| −2 | 2 | 2 | 0,π |
| 4 | 4 | 5 | 0,π |
| −10 | 8 | 7 | 0,π |
| 2 | 16 | 1 | 0,π |
| 4 | 4 | 1 | 0,π |
| 3 | 13 | 5 | 0,π |
| 1 | 3 | 2 | 0,π |

first two were used to define the origin and were kept constant while the other seven were treated as symbolic phases and allowed to assume the values 0 or π radians, giving a total of 128 permutations. Of these, two gave values of $R_\alpha$ <0·23 (ref. 6) while all others had $R_\alpha$ >0·30. The solutions of low $R_\alpha$ were identical, and gave values of 0·22 for an $(E_o - E_c)$ discrepancy factor [6] when the highest 28 independent $E$ map peaks were included as point atoms with atomic numbers proportional to the square roots of the peak heights. The asymmetric unit was found to consist of two half-molecules from which complete molecules were generated by the action of the crystallographic two-fold axis (Figure 1). The positions of these 28 atoms were refined by two cycles of full-matrix least-squares, minimising $\Sigma w|F_o - kF_c|^2$ Scattering factors were from ref. 7 and weights were given by $w = \{\sigma(F)\cdot[2F_{min.} + F_o + 2F_o^2/F_{max.}]\}^{-1}$. The discrepancy factor $R$ was reduced to 0·12 and a difference map indicated the positions of the 20 hydrogen atoms among the 24 highest peaks. Refinement was continued varying positional parameters, anisotropic thermal parameters for the carbon atoms, a single overall isotropic thermal parameter for the hydrogen atoms, and an overall scale factor, a total of 314 parameters. Since the dimensions of the computer program used were limited to 300 variables, it was necessary to vary different combinations of parameters in successive cycles. Full convergence was reached after four cycles. Final values of $R$ and the weighted factor, $R'$, were 0·060 and 0·070 respectively.* Table 3 shows an analysis of variance computed at this stage. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20779 (12 pp., 1 microfiche).† There were no peaks greater than 0·15 eÅ$^{-3}$ on the

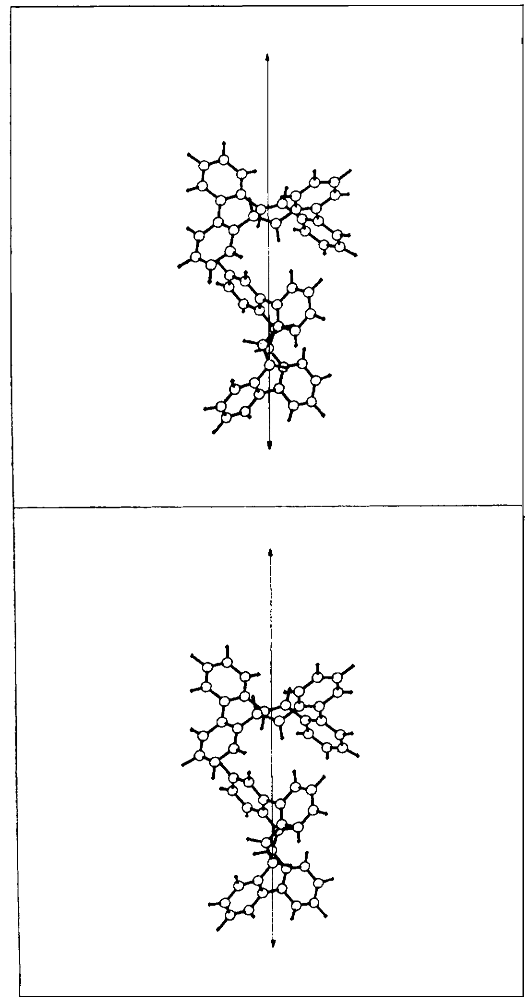


FIGURE 1 Stereoview of the two independent molecules showing their relation to the crystallographic two-fold axis

* $R' = \{\Sigma w|F_o - F_c|^2/\Sigma w|F_o|^2\}^{\frac{1}{2}}$.

† See Notice to Authors No. 7, in *J.C.S. Dalton*, 1972, Index issue.

[5] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1970, *B*, **26**, 274.

[6] R. C. Pettersen, P. J. Roberts, G. M. Sheldrick, N. W. Isaacs, and O. Kennard, preceding paper.

[7] D. Cromer and J. Mann, *Acta Cryst.*, 1968, *A*, **24**, 321.

TABLE 3

Analysis of variance *

(*a*) Ranges of sin θ

| | 0·00—0·39 | 0·39—0·49 | 0·49—0·57 | 0·57—0·63 | 0·63—0·68 | 0·68—0·73 | 0·73—0·77 | 0·77—0·82 | 0·82—0·86 | 0·86—0·90 |
|---|---|---|---|---|---|---|---|---|---|---|
| *N* | 250 | 237 | 257 | 238 | 234 | 260 | 225 | 289 | 226 | 200 |
| *V* | 100 | 114 | 146 | 128 | 83 | 131 | 110 | 119 | 108 | 120 |

(*b*) Ranges of $\sqrt{(F/F_{max})}$

| | 0·00—0·14 | 0·14—0·16 | 0·16—0·18 | 0·18—0·20 | 0·20—0·22 | 0·22—0·25 | 0·25—0·28 | 0·28—0·33 | 0·33—0·40 | 0·40—1·00 |
|---|---|---|---|---|---|---|---|---|---|---|
| *N* | 304 | 241 | 261 | 221 | 209 | 271 | 202 | 266 | 226 | 215 |
| *V* | 159 | 111 | 124 | 123 | 103 | 101 | 146 | 74 | 133 | 48 |

(*c*) By parity groups and zones

| | *ggg* | *uug* | *ggu* | *uuu* | 0*kl* | *h*0*l* | *hk*0 | all |
|---|---|---|---|---|---|---|---|---|
| *N* | 676 | 578 | 581 | 581 | 92 | 103 | 136 | 2461 |
| *V* | 101 | 108 | 114 | 143 | 123 | 110 | 110 | 117 |

* *N* is the number of reflexions in the group and $V = 10^2 \times M\Sigma w|F_o - F_c|^2/N\Sigma w$, where *M* is the total number of reflexions.

TABLE 4

Final fractional co-ordinates ($\times 10^3$ for hydrogen, $\times 10^4$ for carbon)

| Molecule A | | | | Molecule B | | | |
|---|---|---|---|---|---|---|---|
| | *x*/*a* | *y*/*b* | *z*/*c* | | *x*/*a* | *y*/*b* | *z*/*c* |
| C(1) | 1651(2) | 3746(2) | 2137(2) | C(15) | 374(1) | 765(1) | 2871(2) |
| C(2) | 2300(2) | 3237(2) | 2088(3) | C(16) | 901(2) | 1411(2) | 2881(2) |
| C(3) | 2265(2) | 2632(2) | 1404(3) | C(17) | 1602(2) | 1442(2) | 3532(2) |
| C(4) | 1570(2) | 2527(2) | 742(3) | C(18) | 1791(2) | 825(2) | 4181(2) |
| C(5) | 922(2) | 3026(2) | 768(2) | C(19) | 1273(2) | 183(2) | 4186(2) |
| C(6) | 947(2) | 3646(2) | 1454(2) | C(20) | 559(1) | 140(1) | 3540(2) |
| C(7) | 257(2) | 4184(2) | 1427(2) | C(21) | 23(2) | −548(1) | 3593(2) |
| C(8) | −500(2) | 3943(2) | 1427(2) | C(22) | 250(2) | −1310(2) | 3553(2) |
| C(9) | −1185(2) | 4486(2) | 1446(2) | C(23) | −281(1) | −2010(1) | 3548(2) |
| C(10) | −1313(2) | 5111(2) | 773(2) | C(24) | −802(2) | −2059(2) | 4243(2) |
| C(11) | −1955(2) | 5621(2) | 745(3) | C(25) | −1282(2) | −2721(2) | 4299(2) |
| C(12) | −2492(2) | 5521(2) | 1395(3) | C(26) | −1255(2) | −3353(2) | 3656(3) |
| C(13) | −2385(2) | 4904(2) | 2069(3) | C(27) | −754(2) | −3311(2) | 2968(2) |
| C(14) | −1732(2) | 4385(2) | 2112(2) | C(28) | −261(1) | −2645(1) | 2888(2) |
| H(2) | 284(2) | 332(2) | 261(2) | H(16) | 78(2) | 188(2) | 234(2) |
| H(3) | 274(2) | 229(2) | 130(2) | H(17) | 199(2) | 189(2) | 356(2) |
| H(4) | 154(2) | 207(2) | 23(2) | H(18) | 233(2) | 84(2) | 466(2) |
| H(5) | 42(2) | 295(2) | 26(2) | H(19) | 137(2) | −26(2) | 461(2) |
| H(7) | 38(2) | 478(2) | 149(2) | H(21) | −60(2) | −43(2) | 362(2) |
| H(8) | −56(2) | 331(2) | 146(2) | H(22) | 84(2) | −142(1) | 338(2) |
| H(10) | −93(2) | 516(2) | 37(3) | H(24) | −77(2) | −159(2) | 473(2) |
| H(11) | −206(2) | 611(2) | 23(2) | H(25) | −168(2) | −274(2) | 479(2) |
| H(12) | −298(2) | 591(2) | 141(2) | H(26) | −163(2) | −384(2) | 369(2) |
| H(13) | −277(2) | 485(2) | 258(2) | H(27) | −72(2) | −371(2) | 245(2) |

final difference Fourier. Final positional and thermal parameters are given in Tables 4 and 5 together with their standard deviations calculated from the last refinement cycle. The final value of the overall isotropic temperature factor (*U*) for the hydrogen atoms was 0·045 Å$^2$. (I) shows the numbering scheme for molecule A. Molecule B is numbered in the same fashion but with 14 added to each number.

## DISCUSSION

*Molecular Conformation*.—As predicted on the basis of chemical evidence,[4] the product has the *trans,trans*-configuration. Although there are theoretically three possible arrangements for the *trans*-double bonds [(I)—(III)] only (I) and (III) satisfy steric requirements for non-bonded interactions. In the present study, both molecules are of type (I). Tables 6—8 give the molecular geometry in terms of bond lengths, valency angles and torsion angles. No significant differences are observed between the bond lengths and valency angles of this isomer and those of the *cis,trans*-isomer.[2] Although the molecule may be thought of as a derivative of [12]-annulene, the requirement of *cis,cis,trans,cis,cis,trans*-configurations for alternate bonds around the twelve-membered ring causes severe distortion from planarity and hence from aromaticity. This is manifested by the mean torsion angles C(1)–C(6)–C(7)–C(8) and C(9)–C(14)–C(1)–C(6) (130·0 and 54·5°) and by the shortening of the C(7)–C(8) bond length to 1·334 Å (mean from two molecules), close to 1·337 Å, the expected value[8] for a localized double-bond. Torsion angles at the *trans*-double bonds are 177·0 and 176·3°. The four phenyl rings are strictly planar with root-mean-square deviations from the calculated plane ranging from 0·003 to 0·005 Å. Carbon atoms substituent to the rings are displaced an average of 0·037 Å from the calculated plane. Because of this loss of aromaticity at C(1) and C(6), C–C bond lengths for the three bonds most remote from the [12]-annulene system are shorter (Figure 2) and the other three are slightly longer than the expected aromatic bond-

[8] *Chem. Soc. Special Publ.*, No. 18, 1965.

TABLE 5

Anisotropic temperature factors (Å$^2$ × 10$^3$)

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 56(2) | 42(1) | 51(2) | 3(1) | 11(1) | 1(1) |
| C(2) | 56(2) | 52(2) | 68(2) | 5(2) | 6(2) | 8(1) |
| C(3) | 68(2) | 56(2) | 83(2) | −4(2) | 15(2) | 15(2) |
| C(4) | 81(2) | 52(2) | 69(2) | −8(2) | 22(2) | 9(2) |
| C(5) | 64(2) | 54(2) | 55(2) | −5(1) | 13(1) | 2(1) |
| C(6) | 57(2) | 45(1) | 46(2) | −1(1) | 14(1) | 2(1) |
| C(7) | 58(2) | 48(2) | 52(2) | −3(1) | 10(1) | 2(1) |
| C(8) | 58(2) | 51(2) | 52(2) | 1(1) | 8(1) | 4(1) |
| C(9) | 50(1) | 49(2) | 49(2) | −3(1) | 4(1) | 1(1) |
| C(10) | 59(2) | 58(2) | 54(2) | 7(1) | 7(1) | 5(1) |
| C(11) | 71(2) | 59(2) | 68(2) | 10(2) | 3(2) | 9(2) |
| C(12) | 61(2) | 56(2) | 75(2) | −2(2) | 7(2) | 11(2) |
| C(13) | 59(2) | 52(2) | 63(2) | −4(1) | 9(2) | 5(1) |
| C(14) | 53(2) | 44(1) | 52(2) | −5(1) | 7(1) | −1(1) |
| C(15) | 58(1) | 57(1) | 57(1) | −1(1) | 14(1) | −1(1) |
| C(16) | 64(1) | 60(1) | 71(2) | 0(1) | 16(1) | −7(1) |
| C(17) | 66(2) | 63(2) | 86(2) | −8(1) | 16(1) | −17(1) |
| C(18) | 61(2) | 71(2) | 73(2) | −12(1) | 7(1) | −11(1) |
| C(19) | 63(1) | 59(1) | 60(2) | −3(1) | 11(1) | −3(1) |
| C(20) | 56(1) | 54(1) | 57(1) | −9(1) | 12(1) | −4(1) |
| C(21) | 59(1) | 58(1) | 65(2) | −1(1) | 8(1) | −3(1) |
| C(22) | 56(1) | 59(1) | 67(2) | 2(1) | 9(1) | −4(1) |
| C(23) | 50(1) | 55(1) | 52(1) | 3(1) | 2(1) | −2(1) |
| C(24) | 62(1) | 66(2) | 59(2) | 4(1) | 10(1) | −3(1) |
| C(25) | 65(2) | 75(2) | 78(2) | 12(1) | 19(1) | −6(1) |
| C(26) | 65(2) | 67(2) | 99(2) | 8(2) | 16(2) | −13(1) |
| C(27) | 59(1) | 59(2) | 86(2) | −1(1) | 9(1) | −7(1) |
| C(28) | 49(1) | 57(1) | 60(2) | 3(1) | 1(1) | 2(1) |

Coefficients in the temperature factor expression:
$\exp[-2\pi^2(U_{11}h_2a^{*2} + U_{22}k^2b^{*}{}_2 + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

TABLE 6

Bond lengths (Å) with estimated standard deviations in parentheses. Primed atoms are at $-x, y, \frac{1}{2} - z$

| Molecule A | | Molecule B | |
|---|---|---|---|
| C(1)–C(2) | 1·394(4) | C(15)–C(16) | 1·394(3) |
| C(1)–C(6) | 1·411(4) | C(15)–C(20) | 1·400(3) |
| C(2)–C(3) | 1·378(5) | C(16)–C(17) | 1·376(4) |
| C(3)–C(4) | 1·386(5) | C(17)–C(18) | 1·372(4) |
| C(4)–C(5) | 1·376(4) | C(18)–C(19) | 1·382(4) |
| C(5)–C(6) | 1·401(4) | C(19)–C(20) | 1·390(3) |
| C(9)–C(10) | 1·394(4) | C(23)–C(24) | 1·394(3) |
| C(9)–C(14) | 1·404(4) | C(23)–C(28) | 1·403(3) |
| C(10)–C(11) | 1·371(4) | C(24)–C(25) | 1·378(4) |
| C(11)–C(12) | 1·375(5) | C(25)–C(26) | 1·385(4) |
| C(12)–C(13) | 1·383(5) | C(26)–C(27) | 1·363(4) |
| C(13)–C(14) | 1·394(4) | C(27)–C(28) | 1·399(3) |
| Mean C–C (phenyl) 1·39(1) | | | |
| C(6)–C(7) | 1·463(4) | C(20)–C(21) | 1·468(3) |
| C(8)–C(9) | 1·470(4) | C(22)–C(23) | 1·470(3) |
| C(7)–C(8) | 1·335(4) | C(21)–C(22) | 1·332(3) |
| C(1)–C(14′) | 1·481(4) | C(15)–C(15′) | 1·502(5) |
| | | C(28)–C(28′) | 1·483(5) |
| C(2)–H(2) | 1·08(3) | C(16)–H(16) | 1·08(3) |
| C(3)–H(3) | 1·01(3) | C(17)–H(17) | 0·99(3) |
| C(4)–H(4) | 1·03(3) | C(18)–H(18) | 1·04(3) |
| C(5)–H(5) | 1·02(3) | C(19)–H(19) | 0·94(3) |
| C(7)–H(7) | 1·02(3) | C(21)–H(21) | 1·08(3) |
| C(8)–H(8) | 1·06(3) | C(22)–H(22) | 1·06(3) |
| C(10)–H(10) | 0·92(3) | C(24)–H(24) | 1·03(3) |
| C(11)–H(11) | 1·08(3) | C(25)–H(25) | 1·02(3) |
| C(12)–H(12) | 1·05(3) | C(26)–H(26) | 1·04(3) |
| C(13)–H(13) | 1·03(3) | C(27)–H(27) | 0·98(3) |

Mean C–H 1·05(3)

length of 1·394 Å.[8] Internal valence angles at C(2) and C(5) are larger and the other four are smaller than the standard value of 120°. A similar pattern was reported for the *cis,trans*-isomer.[2]

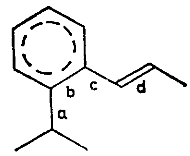
TABLE 7

Valency angles (°) with estimated standard deviations in parentheses

| Molecule A | | Molecule B | |
|---|---|---|---|
| C(6)–C(1)–C(2) | 118·7(3) | C(20)–C(15)–C(16) | 119·4(2) |
| C(14′)–C(1)–C(2) | 118·8(3) | C(16)–C(15)–C(15′) | 118·3(2) |
| C(14′)–C(1)–C(6) | 122·5(3) | C(20)–C(15)–C(15′) | 122·3(2) |
| C(3)–C(2)–C(1) | 121·6(3) | C(17)–C(16)–C(15) | 121·2(3) |
| C(4)–C(3)–C(2) | 119·6(3) | C(18)–C(17)–C(16) | 119·7(3) |
| C(5)–C(4)–C(3) | 120·0(3) | C(19)–C(18)–C(17) | 119·9(3) |
| C(6)–C(5)–C(4) | 121·3(3) | C(20)–C(19)–C(18) | 121·6(3) |
| C(5)–C(6)–C(1) | 118·7(3) | C(19)–C(20)–C(15) | 118·3(2) |
| C(7)–C(6)–C(1) | 121·8(3) | C(21)–C(20)–C(15) | 122·6(2) |
| C(7)–C(6)–C(5) | 119·4(3) | C(21)–C(20)–C(19) | 119·1(2) |
| C(8)–C(7)–C(6) | 124·5(3) | C(22)–C(21)–C(20) | 124·3(2) |
| C(9)–C(8)–C(7) | 124·3(3) | C(23)–C(22)–C(21) | 125·6(2) |
| C(10)–C(9)–C(8) | 119·6(3) | C(24)–C(23)–C(22) | 119·0(2) |
| C(14)–C(9)–C(8) | 121·9(3) | C(28)–C(23)–C(22) | 122·1(2) |
| C(14)–C(9)–C(10) | 118·4(3) | C(28)–C(23)–C(24) | 118·8(2) |
| C(11)–C(10)–C(9) | 121·8(3) | C(25)–C(24)–C(23) | 121·1(3) |
| C(12)–C(11)–C(10) | 119·7(3) | C(26)–C(25)–C(24) | 120·1(3) |
| C(13)–C(12)–C(11) | 119·8(3) | C(27)–C(26)–C(25) | 119·4(3) |
| C(14)–C(13)–C(12) | 121·1(3) | C(28)–C(27)–C(26) | 122·0(3) |
| C(13)–C(14)–C(9) | 119·0(3) | C(27)–C(28)–C(23) | 118·5(2) |
| C(13)–C(14)–C(1′) | 118·0(3) | C(27)–C(28)–C(28′) | 118·5(2) |
| C(9)–C(14)–C(1′) | 123·0(3) | C(23)–C(28)–C(28′) | 123·0(2) |
| H(2)–C(2)–C(1) | 118(2) | H(16)–C(16)–C(15) | 120(2) |
| H(2)–C(2)–C(3) | 120(2) | H(16)–C(16)–C(17) | 119(1) |
| H(3)–C(3)–C(2) | 124(2) | H(17)–C(17)–C(16) | 124(2) |
| H(3)–C(3)–C(4) | 116(2) | H(17)–C(17)–C(18) | 117(2) |
| H(4)–C(4)–C(3) | 120(2) | H(18)–C(18)–C(17) | 120(2) |
| H(4)–C(4)–C(5) | 120(2) | H(18)–C(18)–C(19) | 120(2) |
| H(5)–C(5)–C(4) | 119(2) | H(19)–C(19)–C(18) | 124(2) |
| H(5)–C(5)–C(6) | 120(2) | H(19)–C(19)–C(20) | 115(2) |
| H(7)–C(7)–C(6) | 117(2) | H(21)–C(21)–C(20) | 118(1) |
| H(7)–C(7)–C(8) | 118(2) | H(21)–C(21)–C(22) | 118(1) |
| H(8)–C(8)–C(7) | 114(2) | H(22)–C(22)–C(21) | 117(1) |
| H(8)–C(8)–C(9) | 122(2) | H(22)–C(22)–C(23) | 116(1) |
| H(10)–C(10)–C(9) | 115(2) | H(24)–C(24)–C(23) | 116(2) |
| H(10)–C(10)–C(11) | 123(2) | H(24)–C(24)–C(25) | 123(2) |
| H(11)–C(11)–C(10) | 123(2) | H(25)–C(25)–C(24) | 121(2) |
| H(11)–C(11)–C(12) | 117(2) | H(25)–C(25)–C(26) | 119(2) |
| H(12)–C(12)–C(11) | 122(2) | H(26)–C(26)–C(25) | 120(2) |
| H(12)–C(12)–C(13) | 118(2) | H(26)–C(26)–C(27) | 121(2) |
| H(13)–C(13)–C(12) | 120(2) | H(27)–C(27)–C(26) | 126(2) |
| H(13)–C(13)–C(14) | 119(2) | H(27)–C(27)–C(28) | 112(2) |

TABLE 8

**Torsion angles** (deg.)




| | Molecule A | | Molecule B | |
|---|---|---|---|---|
| a | 55·2 | | −56·1 | −51·4 |
| b | 1·7 | 2·0 | −2·4 | −3·4 |
| c | −129·2 | −130·4 | 127·0 | 133·5 |
| d | 177·0 | | −176·3 | |

Because the crystal structure contains molecules bisected by two-fold axes in two directions mutually at 90°, the free molecule must have $D_2$ (222) symmetry. The results of an analysis of bond lengths and valency and torsion angles which would be equivalent under this site symmetry are shown in Figure 2 and Table 8. No individual bond length of a supposedly equivalent group differs from the mean value for its group by more than 3·0 times the standard deviation of the individual bond length, while only one valency angle differs from the mean value for its group by $>3{\cdot}0\sigma$. Such agreement does not however hold for the torsion angles (Table 8) where differences as large as 6·5° occur. Such deviations presumably accommodate packing forces encountered upon crystallization.

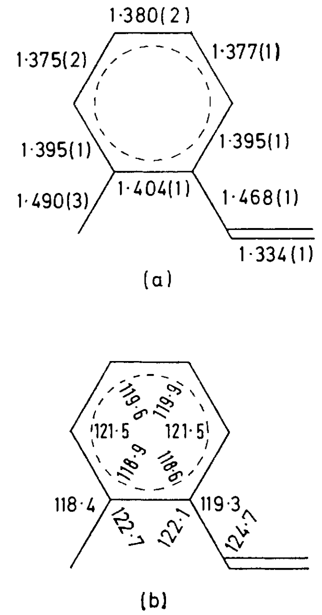



FIGURE 2 Mean values of (a) bond lengths and (b) valency angles in terms of $D_2$ symmetry; mean $\sigma$ are given in parentheses for bond lengths, for valency angles mean $\sigma$ all 0·1°

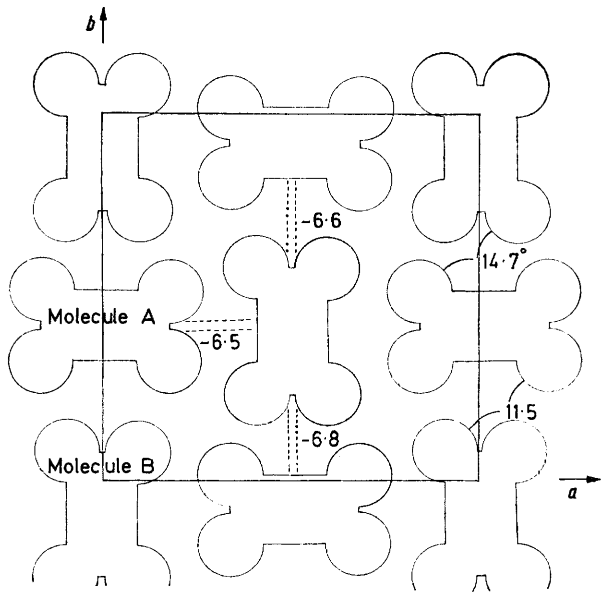



FIGURE 3 Schematic representation of the packing pattern viewed on the *ab* plane showing, in the centre of the diagram, the van der Waals interaction energies (kcal), and on the right the angles between the normals to the calculated mean plane of the phenyl rings in close contact

*Extended Crystal Structure*.—Figures 3 and 4 show schematic representations of the packing pattern as viewed on the *ab* and *bc* planes respectively. Interaction energies are calculated from empirical potentials [9] and although their exact absolute magnitudes are not necessarily significant, they have been used to predict several crystal structures [10,11] and to determine the most significant interactions in others.[12]

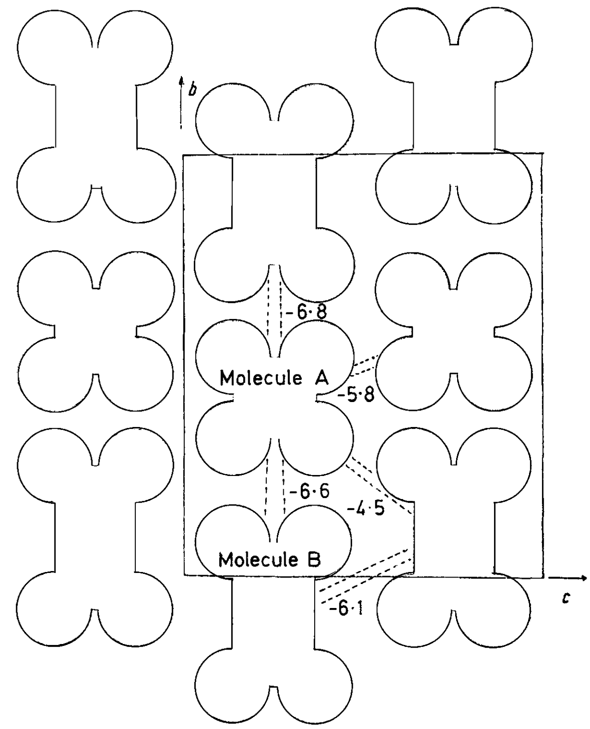



FIGURE 4 Schematic packing diagram viewed on the *bc* plane showing van der Waals interaction energies (kcal)

Strong van der Waals interactions occur in three directions, principally due to the parallel arrangement of phenyl rings. Molecules A and B are linked into an infinite chain along the crystallographic two-fold axis parallel to *b* with energies of −6·6 (A–B) and −6·8 A–B(1010)) kcal. The numbers in parentheses are the symmetry operator number ($1 = x,y,z$; $2 = -x,-y,-z$) and translation numbers in the *a*, *b*, and *c* directions. The angles between the calculated mean planes of the phenyl rings in close proximity at these contacts are 11·5 and 14·7°. The distances between the centres of these rings are 5·99 and 5·77 Å. Although these distances are remote from the minimum of the C–C potential-energy curve, the combined effect of four such ring overlaps per molecule is sufficient to stabilize this packing arrange-

[9] E. Giglio, *Nature*, 1969, **222**, 339.
[10] V. M. Coiro, P. Giacomello, and E. Giglio, *Acta Cryst.*, 1971, *B*, **27**, 2112.
[11] A. Damiani, E. Giglio, A. M. Liquori, and L. Mazzarella, *Nature*, 1967, **215**, 1161.
[12] W. D. S. Motherwell and N. W. Isaacs, *J. Mol. Biol.*, 1972, **71**, 231.

ment. This chain is extended infinitely in the *a* direction by interactions of $-6{\cdot}5$ kcal of the type A–B($1\frac{1}{2}\frac{1}{2}0$). This pattern (Figure 3) of packing illustrates why the *a* and *b* cell-dimensions are nearly equal and why the crystal structure is *C* centred.

Figure 4 shows how the *ab* sheet structure is extended infinitely in the *c* direction with interactions of energies $-6{\cdot}1$ [B–B(2000)], $-4{\cdot}5$ [A–B(2000)], and $-5{\cdot}8$ [A–A(2010)] kcal. The crystal structure is thus held together by strong van der Waals potential forces acting approximately isotropically in the three unit-cell directions. This explains the difficulty of cleavage and high m.p. (301 °C) observed for this compound.

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