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anti-Tetramantane, a Large Diamondoid Fragment

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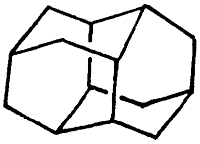
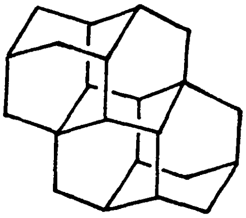
Abstract. $C_{22}H_{28}$, M_r = 292·47, monoclinic, a = 6·495 (2), b = 11·558 (3), c = 10·330 (1) Å, β = 98·22 (1)°, V = 767·5 Å^3, Z = 2, D_x = 1·27 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·35 cm^{-1}, $F(000)$ = 320, space group $P2_1/n$ (alternative setting of C^5_{2h}, No. 14) from systematic absences $0k0$, $k = 2n + 1$, $h0l$, $h + l = 2n + 1$. Full-matrix least-squares refinement using 788 observed reflexions has resulted in a final R value of 0·040. The molecule is centrosymmetric, the carbon skeleton being a portion of the diamond lattice.

Introduction. Our examination of crystals of the product of the double homologation of diamantane (I) has proven them to be *anti*-tetramantane (II) (Burns, Mitchell, McKervey, Rooney, Ferguson & Roberts, 1976).



(I)



(II)

A small crystal of dimensions 0·2 × 0·3 × 0·75 mm was used in the analysis. Intensity data were measured using graphite-monochromated Mo $K\alpha$ radiation and a Hilger & Watts Y290 four-circle diffractometer operated in the $\theta/2\theta$ step scan mode. Seventy steps, each of 0·01° (θ) and 0·5 s duration were taken through each reflexion. Background counts of 17·5 s were measured at both ends of the scan. Each intensity was assigned a σ value using the formula $\sigma^2(I) = S + B + (0{\cdot}05S)^2$ where S is the total scan count, B is the sum of the two backgrounds and $I = S - B$. Lorentz and polarization corrections (including a term to allow for the monochromator) were applied to 1976 reflexions with θ(Mo $K\alpha$) ≤ 23°. No absorption correction was applied as this was negligible with the crystal used and the low value of μ (0·35 cm^{-1}). Systematic absences having been eliminated and reflexions with $I < 3\sigma(I)$ classified as unobserveds, the remaining reflexions were averaged where appropriate. This gave R_e* = 0·043 and left 790 unique observed reflexions.

The structure was solved by direct methods using the programs of Sheldrick (1976). The starting set was selected automatically and phases were generated for 178 reflexions with E > 1·2. The best E map on the basis of several criteria gave the positions of the 11 C atoms of the asymmetric unit as the 11 highest peaks. Full-matrix least-squares refinement {with weights derived from the counting statistics, $\sqrt{w} = [1/\sigma^2(F)]^{1/2}$} of 11 anisotropic C atoms and 14 isotropic H atoms (initially located in calculated positions) led to R = 0·049. Removal of the 110 and 020 reflexions because of suspected extinction problems, followed by two further cycles of refinement, led to convergence and final values of R and R_w† of 0·040 and 0·052 respec-

Table 1. *Final fractional coordinates* (× 10^4 *for* C *and* 10^3 *for* H)

	x	y	z
C(1)	391 (5)	1956 (2)	5313 (2)
C(2)	241 (4)	1060 (2)	4219 (2)
C(3)	395 (5)	1618 (2)	2892 (3)
C(4)	230 (4)	715 (3)	1811 (2)
C(5)	−1847 (5)	91 (3)	1731 (3)
C(6)	−2002 (4)	−491 (2)	3037 (2)
C(7)	233 (4)	1378 (2)	6624 (2)
C(8)	−1849 (4)	743 (2)	6570 (2)
C(9)	1999 (4)	161 (2)	4533 (2)
C(10)	−1840 (3)	408 (2)	4145 (2)
C(11)	2001 (5)	−158 (3)	2115 (3)
H(1*A*)	−73 (4)	256 (2)	511 (2)
H(1*B*)	170 (5)	234 (2)	533 (2)
H(3*A*)	173 (5)	200 (2)	297 (2)
H(3*B*)	−74 (5)	217 (2)	267 (3)
H(4)	30 (5)	105 (2)	95 (3)
H(5*A*)	−202 (5)	−47 (2)	101 (3)
H(5*B*)	−299 (5)	65 (3)	146 (3)
H(6)	−329 (4)	−88 (2)	305 (2)
H(7)	33 (4)	199 (2)	730 (2)
H(8)	−299 (4)	129 (2)	637 (2)
H(9)	333 (4)	52 (2)	455 (2)
H(10)	−294 (4)	99 (2)	394 (2)
H(11*A*)	329 (5)	22 (3)	210 (3)
H(11*B*)	189 (5)	−77 (2)	140 (3)

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* $R_e = \{\Sigma[n\,\Sigma\,\omega(\bar{F} - F)^2]/\Sigma[(n-1)\,\Sigma\,\omega F^2]\}^{1/2}$ where the inner summations are over the n equivalent reflexions averaged to give $\bar{F}$ and the outer summations are over all unique reflexions.

† $R_w = [\Sigma\,w(F_o - F_c)^2/\Sigma\,wF_o^2]^{1/2}$.

Table 2. *Bond lengths* (Å), *with standard deviations in parentheses, and angles* (°) *of the carbon skeleton*

Mean standard deviation of C–C–C angles is 0·2 °.

C(1)–C(2)	1·525 (3)	C(5)–C(6)	1·524 (3)
C(1)–C(7)	1·526 (3)	C(6)–C(10)	1·538 (3)
C(2)–C(3)	1·531 (3)	C(6)–C(7′)	1·542 (4)
C(2)–C(9)	1·544 (3)	C(7)–C(8)	1·533 (3)
C(2)–C(10)	1·540 (3)	C(8)–C(11′)	1·532 (4)
C(3)–C(4)	1·521 (4)	C(8)–C(9′)	1·539 (3)
C(4)–C(5)	1·522 (4)	C(9)–C(10′)	1·532 (3)
C(4)–C(11)	1·529 (4)		

C(2)–C(1)–C(7)	110·8	C(10)–C(6)–C(7′)	108·1
C(1)–C(2)–C(3)	111·8	C(1)–C(7)–C(8)	110·4
C(1)–C(2)–C(9)	109·5	C(1)–C(7)–C(6′)	110·5
C(3)–C(2)–C(9)	109·3	C(8)–C(7)–C(6′)	108·3
C(1)–C(2)–C(10)	109·4	C(7)–C(8)–C(9′)	108·3
C(3)–C(2)–C(10)	109·4	C(7)–C(8)–C(11′)	110·4
C(9)–C(2)–C(10)	107·4	C(9′)–C(8)–C(11′)	110·6
C(2)–C(3)–C(4)	111·2	C(2)–C(9)–C(8′)	109·6
C(3)–C(4)–C(5)	109·5	C(2)–C(9)–C(10′)	109·5
C(3)–C(4)–C(11)	109·3	C(8′)–C(9)–C(10′)	111·3
C(5)–C(4)–C(11)	109·5	C(2)–C(10)–C(6)	109·5
C(4)–C(5)–C(6)	109·3	C(2)–C(10)–C(9′)	109·7
C(5)–C(6)–C(10)	110·8	C(6)–C(10)–C(9′)	111·5
C(5)–C(6)–C(7′)	110·7	C(4)–C(11)–C(8′)	109·4

tively. The maximum shift/error ratio was 0·18 for the *y* parameter of H(5*A*). Difference syntheses computed at the conclusion of the refinement showed a general flat topography with no significant features, establishing that the refinement was complete.

Final coordinates with standard deviations calculated from the final refinement cycle are given in Table 1 and details of the molecular geometry are in Table 2.*

Discussion. The crystal structure (Fig. 1) consists of discrete molecules separated by normal van der Waals contacts. Although the molecule (Fig. 2) is only required by space-group symmetry to be centrosymmetric, it conforms to $2/m$ symmetry within the accuracy of the analysis (standard deviations in positional parameters: 0·002–0·003 Å).

Classification of the C–C bond lengths according to degree of substitution (Table 3*a*) reveals a significant trend. The closer one comes to the situation in the diamond lattice, *i.e.* bonding between quaternary C atoms, the larger is the measured bond length. A similar scheme for the valency angles is given in Table 3(*b*). The largest (111·8°) and the smallest (107·4°) angles both occur at the unique quaternary C atom C(2). Both result from the steric interaction between the four H atoms on next-nearest neighbours. Angles of the type CH–CH–CH can be divided into two groups. Those at C(10)–C(6)–C(7′),* C(8)–C(7)–C(6′) and C(7)–C(8)–C(9′) have the H atoms on next-nearest neighbours in the equatorial (and hence non-interfering) positions, while those at C(8′)–C(9)–C(10′) and C(6)–C(10)–C(9′) have next-nearest neighbour H atoms in axial positions. Because the angle at any C atom is dependent upon both the size and orientation of the groups bonded to it, no correlation can be made

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* Temperature factors, dimensions involving H atoms, torsion angles and observed and calculated structure factors, together with an analysis of variance, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32574 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* In the text and tables a primed atom is obtained from the coordinates of Table 1 by the transformation $-x, -y, 1-z$.

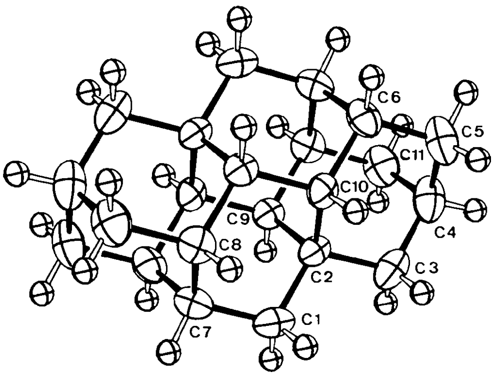

Fig. 2. A view of one molecule of *anti*-tetramantane showing the crystallographic numbering scheme.

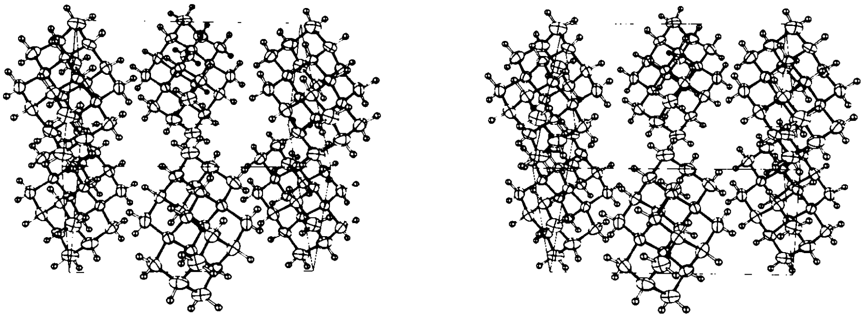

Fig. 1. A stereoscopic drawing of the molecular packing with the *b* axis horizontal.

Table 3. *Classification of bond lengths and angles*

(*a*) Mean bond lengths classified according to degree of substitution (Å)

CH–CH$_2$	1·524 (2)	C–CH$_2$	1·528 (3)	CH–CH	1·537 (2)	C–CH	1·542 (2)

(*b*) Mean valency angles classified according to degree of substitution of the three C atoms (°)

CH–C–CH	107·4 (2)	C–CH–CH	109·6 (1)	C–CH$_2$–CH	111·0 (2)
CH–C–CH$_2$	109·4 (1)	CH–CH–CH (eq.)	108·2 (1)	CH–CH$_2$–CH	109·4 (1)
CH$_2$–C–CH$_2$	111·8 (2)	(axial)	111·4 (1)		
		CH–CH–CH$_2$	110·6 (1)		
		CH$_2$–CH–CH$_2$	109·4 (1)		

between valence angle and the nature of the C substituents alone.

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p-Nitrobenzonitrile

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Abstract. $C_7H_4N_2O_2$, monoclinic, $P2_1$, $a = 12{\cdot}732$ (3), $b = 7{\cdot}058$ (3), $c = 3{\cdot}847$ (2) Å, $\beta = 93{\cdot}670$ (2)°, $D_m = 1{\cdot}430$, $D_c = 1{\cdot}415$ g cm^{-3}, $Z = 2$. The final R value was 0·086 for 708 independent reflexions measured photographically. The molecular dimensions are normal. There is no abnormally short intermolecular contact, but the arrangement of the molecules suggests that there is some contribution from Coulombic interactions, in addition to those involving local dipoles, to the molecular packing.

Introduction. As part of the project to study the effect of polar groups on molecular packing in crystals, the crystal structure of *p*-nitrobenzonitrile was analysed since the values of the dipole moment of benzonitrile and nitrobenzene, both equal to about 4 D, suggested a large contribution from dipolar interactions due to the cyano and nitro groups. Pale-yellow, plate-like crystals elongated along **b** were grown from an ether solution.

Reflexion data were visually estimated from equi-inclination Weissenberg photographs taken around the b and c axes with Ni-filtered Cu $K\alpha$ radiation. Application of the usual corrections gave 708 independent F values. No absorption correction was applied [μ(Cu $K\alpha$) = 9·24 cm^{-1}]. The space group is either $P2_1$ or $P2_1/m$ from the systematic absence: $0k0$, $k = 2n + 1$. The choice of $P2_1$ was verified through successful analysis.

The structure was solved by two-dimensional R-index maps based on the relative orientation of the phenyl ring, obtained from a sharpened Patterson synthesis. The model was refined first by a constrained least-squares method, and subsequently by a full-matrix least-squares method with anisotropic thermal factors, to the final R value of 0·086. The H atoms were included in the structure factor calculations with calculated positions. All the computations were carried

Table 1. *Final positional parameters* (×10^4) *of the non-hydrogen atoms*

	x	y	z
C(1)	1933 (5)	0	2884 (16)
C(2)	3010 (5)	78 (15)	3794 (17)
C(3)	3573 (5)	1685 (15)	3030 (18)
C(4)	3045 (5)	3162 (14)	1304 (16)
C(5)	1973 (6)	3102 (15)	361 (17)
C(6)	1411 (5)	1516 (15)	1185 (18)
C(7)	1343 (6)	−1648 (18)	3761 (21)
N(8)	895 (5)	−2963 (15)	4501 (19)
N(9)	3653 (5)	4887 (14)	537 (16)
O(10)	4556 (5)	5038 (16)	1760 (19)
O(11)	3226 (5)	6041 (14)	−1377 (19)