Table 3. H···O *intermolecular distances* (Å) *and symmetry operations for distances* < 2·6 Å *in* (I) *and* (II)

C—H bonds lengths adjusted to 1·10 Å.

	Distance	Symmetry operation
(II)		
O1···H12	2·27	$x, 1+y, z$
O1′···H12′	2·40	$x, -1+y, z$
O2′···H4	2·45	$\frac{1}{2}+x, -\frac{1}{2}-y, -\frac{1}{2}+z$
O1′···H6	2·45	$-\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
O2′···H2	2·47	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
O4′···H4′	2·54	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
(I)		
O1···H21	2·39	$1-x, 1-y, 1-z$

unusual intermolecular distances; a short list of distances in (I) and (II) is given in Table 3. The packing in both (I) and (II) is ordinary.

A number of density-related parameters together with the percent changes encountered from unsubstituted (I) to nitro-substituted (II) are listed in Table 4. The changes in molecular volume, the surface areas and molecular density are normal for the replacement of H in (I) by NO_2 in (II). There is little net change in the surface area available for intermolecular contacts (accessible surface area) relative to the change in molecular volume. The most interesting parameters in terms of molecular structure and crystal density are in the last three rows. One finds virtually identical percent changes in $\rho_{\rm mol}$ (molecular density) and ρ_x (crystal density from unit-cell volume) and effectively no change in packing coefficient. These data indicate that unit-cell space is utilized with the same efficiency in the crystals of (I) and (II), and that the observed increase in ρ_x is solely the result of an increase in $\rho_{\rm mol}$.

Table 4. *Comparison of several density-related parameters for* (I) *and* (II)

Parameters calculated with *SVDHA* (Zhang, 1985). All C—H lengths are normalized to 1·10 Å. van der Waals radii used are C = 1·70, H = 1·1, N = 1·55, O = 1·52 Å.

	(I)	(II)*	% change
Molecular weight	188·2	233·2	23·9
Molecular volume (Å^3)*	158·3	181·2	14·5
Molecular surface area (Å^2)	181·2	210·2	16·0
Accessible surface area (Å^2)†	71·5	82·8	15·9
Molecular density (g cm^{-3})	1·975	2·136	8·2
Crystal density from unit-cell volume (g cm^{-3})	1·415	1·521	7·5
Packing coefficient‡	0·716	0·712	~0

* Values given for (II) are averages for the two molecules.

† Surface area of a molecule that can be in contact with an external atom with a radius of 1·52 Å.

‡ Molecular volume/unit-cell volume per molecule.

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Structure of 1,5,9-Trinitrobishomopentaprismane

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Abstract. 2,3,8-Trinitrohexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{4,8}.0^{9,12}]dodecane (IV), $C_{12}H_{11}N_3O_6$, $M_r = 293·2$, orthorhombic, $Pna2_1$, $a = 11·467$ (1), $b = 8·756$ (1), $c = 11·9339$ (8) Å, $V = 1198·2$ (4) Å^3, $D_x = 1·625$ g cm^{-3}, $Z = 4$, Cu $K\alpha$, $\lambda = 1·54178$ Å, $\mu = 11·6$ cm^{-1}, $F(000) = 608$, $T = 293$ K, final $R = 0·061$,

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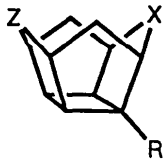
$wR = 0.091$ for 1082 reflections with $I > 3\sigma(I)$. There are no unusual intermolecular distances and the crystal packing is normal. The crystal density of (IV) is only 2·3% larger than that of 1,5-dinitrobishomopentaprismane (III) at 1·589 g cm^{-3} despite a 6·7% higher molecular density of (IV) over (III). An analysis of crystal packing and the calculated crystal packing coefficients indicates that the small crystal-density change is the result of more efficient molecular packing in (III) over (IV), which compensates for the lower molecular density of (III). The molecular shape and polarity of (III) lead to efficient crystal packing.

Introduction. The solid-state density of an energetic material such as a propellant or explosive is one of its more important properties. Characteristics such as detonation velocity and pressure are functions of density as is the quantity of material that can be packed into a limited volume. The principal determinants of crystal density are the molecular density (molecular mass/molecular volume) and the crystal packing efficiency. The volume of a molecule can be calculated by an appropriate overlap-corrected summation of atomic spheres derived from the van der Waals radii. The unit-cell volume includes contributions from both the molecular volume and the unoccupied space between molecules in the crystal. Some years ago, Kitaigorodskii (1961) defined the term 'packing coefficient' (molecular volume/unit-cell volume) as an expression of the crystal packing efficiency. Clearly the most dense crystals, for a series of C—H—N—O-containing molecules, will have both high molecular densities and high packing coefficients.

The replacement of a low-density atom (*e.g.* hydrogen) by a high-density atom or group (*e.g.* NO_2) usually produces an increase in the crystal density because of an increase in the molecular density. For a typical compound of molecular weight 200, replacement of H by NO_2 would lead to a density increase of 0·05–0·1 g cm^{-3}. Such a change in the crystal density, however, could be mitigated or possibly reversed if the high-density replacement group diminished the crystal packing efficiency. The influence of an additional nitro-group substituent on the crystal densities of a series of [4]peristylane and bishomopentaprismane derivatives has recently been investigated by Shen & Paquette (1989), who showed for several pairs of compounds that replacement of a basal H atom by a nitro group does not lead invariably to a concomitant increase in crystal density. For example, the change in density from the [4]peristylane derivative (I) (1·415 g cm^{-3}) to (II) (1·521 g cm^{-3}) is typical, whereas there is a smaller decrease in crystal density accompanying nitro substitution from bishomopentaprismane (III) to (IV) (1·589 to 1·625 g cm^{-3}). We have undertaken crystal structure determinations of several of the [4]peristylanes and bishomopentaprismanes to enable a detailed study to be made of the crystal packing effects of basal nitro-group substitution. In this paper, we report the structure of (IV) and compare the structure with that of (III) determined by Paquette, Fisher & Engel (1985).



(I): $X = Z =$ C=O, $R =$ H
(II): $X = Z =$ C=O, $R = NO_2$
(III): X—$Z = O_2N$—C—C—NO_2, $R =$ H
(IV): X—$Z = O_2N$—C—C—NO_2, $R = NO_2$

Experimental. (IV): 0·26 × 0·33 × 0·33 mm block-like crystal; Enraf–Nonius CAD-4 diffractometer with incident-beam graphite monochromator; cell parameters and crystal orientation from 25 automatically centered reflections in the range $12.8 < \theta < 38.7°$; 2θ–θ scans over θ range of $1.5(1.05 + 0.14\tan\theta)°$; variable θ scan speed of 1·50–8·24° min^{-1}; each scan recorded in 96 steps with two outermost 16-step intensity blocks used for background determination; diffractometer controlled with Digital Equipment Corporation MicroVAX II computer and standard Enraf–Nonius programs (version 5.0); eight standard reflections monitored at 1 h intervals of X-ray exposure, 1·4 to 2·7% intensity variation, 1·9% average, correction applied; ψ-scan absorption correction applied, transmission-factor range 0·897–1·000, average 0·932; $\theta_{\max}$ of 70°, hemisphere of data collected with *hkl's* selected to maintain diffractometer χ angle within 0–90° range; 4663 total data measured, 1270 unique data, 1082 data with $I > 3\sigma(I)$, $R_{\rm int} = 0.023$ for 245 twice-measured and 988 quadruply-measured data. All crystallographic calculations performed with the *TEXSAN* (Molecular Structure Corporation, 1989) program system on DEC MicroVAX II or VAXStation II computers; structure solved with the *SIR* direct-methods program (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) incorporated in *TEXSAN*. Full-matrix least-squares refinement, $\sum[1/\sigma^2(F_o)(F_o - F_c)^2]$ minimized, reflections with $I < 3\sigma(I)$ excluded from refinement, correction for secondary isotropic extinction (Zachariasen, 1968) applied, $g = 0.148\ (6) \times 10^{-6}$; anisotropic temperatue factors for C, O and N; H atoms positioned from the C-atom framework and refined with individual isotropic temperature factors; 234 total variables; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 155–

Table 1. *Fractional coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$B = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B
O1	0·1859 (7)	0·1615 (9)	1·0617	8·9 (4)
O2	0·0913 (7)	0·1647 (7)	0·9099 (8)	8·7 (3)
O3	−0·0229 (6)	0·418 (1)	1·0507 (9)	9·9 (4)
O4	−0·0734 (5)	0·470 (1)	0·882 (1)	9·0 (4)
O5	0·5178 (5)	0·6162 (6)	0·7685 (9)	7·3 (3)
O6	0·4638 (4)	0·4060 (5)	0·6938 (7)	5·1 (2)
N1	0·1604 (4)	0·2197 (5)	0·9747 (7)	4·3 (2)
N2	0·0009 (5)	0·4610 (7)	0·9557 (8)	5·3 (2)
N3	0·4526 (4)	0·5089 (5)	0·7604 (8)	4·3 (2)
C1	0·2154 (4)	0·3695 (5)	0·9440 (7)	3·3 (2)
C2	0·2727 (4)	0·3643 (5)	0·8273 (7)	3·1 (2)
C3	0·1760 (5)	0·4131 (6)	0·7463 (7)	4·1 (2)
C4	0·1451 (5)	0·5576 (6)	0·8096 (7)	4·2 (2)
C5	0·1253 (4)	0·5047 (5)	0·9314 (8)	3·8 (2)
C6	0·1739 (5)	0·6243 (6)	1·0154 (8)	4·6 (2)
C7	0·2256 (6)	0·5271 (8)	1·1096 (8)	5·2 (3)
C8	0·3018 (4)	0·4305 (6)	1·0322 (7)	4·0 (2)
C9	0·3488 (4)	0·5069 (5)	0·8363 (7)	3·3 (2)
C10	0·2617 (5)	0·6418 (5)	0·8241 (8)	4·3 (2)
C11	0·2783 (6)	0·6812 (6)	0·9493 (8)	4·8 (2)
C12	0·3670 (5)	0·5496 (7)	0·9614 (7)	4·1 (2)

175); min. and max. $\Delta\rho$ of $-0{\cdot}21$ and $0{\cdot}46$ e Å^{-3}; max. Δ/σ in final least-squares cycle 0·09; R, wR and S 0·061, 0·091 and 3·4, respectively. Atomic coordinates are listed in Table 1.* The *PLOTMD* program (Luo, Ammon & Gilliland, 1989) was used to display the *ORTEP* drawings (Johnson, 1965) on a VAX-Station II monitor, label the drawings and prepare print files for a Hewlett–Packard Laser-Jet II printer.

Discussion. An *ORTEP* drawing is shown in Fig. 1 and bond lengths, bond angles and selected torsion angles are given in Table 2. Comparable values are observed in the crystal structures of other bishomopentaprismanes [*i.e.* (III), Paquette, Fischer & Engel (1985); (V), (VI), Paquette, Nakamura & Engel (1986); (VII), Ammon & Du (1988)]. It should be noted that the crystal structure determination of (III) was performed at 133 K. Table 3 summarizes the average lengths of the three principal types of C—C bonds in (III)–(VII). With the exclusion of (VII), which appears to be somewhat anomalous, the C1—C5 bonds are longest at 1·58–1·59 Å followed by the basal cyclobutane bonds at 1·55–1·56 Å and other bonds at 1·53–1·54 Å. The orientations of the C9-linked nitro groups in (II) and (IV) are quite different: the O—N3—C9—C2 dihedral angles, for example, are −73·6 and 4·2° in (II) and (IV), respectively.

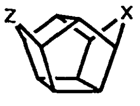
Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

O1—N1	1·188 (7)	C2—C9	1·530 (6)
O2—N1	1·212 (7)	C3—C4	1·526 (9)
O3—N2	1·21 (1)	C4—C10	1·532 (8)
O4—N2	1·227 (9)	C4—C5	1·539 (7)
O5—N3	1·213 (7)	C5—C6	1·555 (8)
O6—N3	1·198 (7)	C6—C11	1·519 (9)
N1—C1	1·500 (7)	C6—C7	1·54 (1)
N2—C5	1·509 (8)	C7—C8	1·524 (9)
N3—C9	1·491 (6)	C8—C12	1·525 (8)
C1—C2	1·542 (6)	C9—C10	1·551 (7)
C1—C8	1·542 (7)	C9—C12	1·560 (7)
C1—C5	1·578 (7)	C10—C11	1·546 (9)
C2—C3	1·529 (7)	C11—C12	1·55 (1)

O1—N1—O2	122·8 (6)	C4—C5—C6	110·7 (5)
O1—N1—C1	119·2 (5)	C4—C5—C1	103·1 (4)
O2—N1—C1	118·0 (5)	C6—C5—C1	102·0 (4)
O3—N2—O4	121·4 (6)	C11—C6—C7	105·5 (5)
O3—N2—C5	118·4 (6)	C11—C6—C5	99·6 (5)
O4—N2—C5	120·2 (6)	C7—C6—C5	103·6 (5)
O6—N3—O5	124·2 (5)	C8—C7—C6	94·4 (5)
O6—N3—C9	119·1 (5)	C7—C8—C12	104·5 (5)
O5—N3—C9	116·7 (5)	C7—C8—C1	103·6 (4)
N1—C1—C2	112·0 (4)	C12—C8—C1	100·2 (4)
N1—C1—C8	114·0 (4)	N3—C9—C2	114·8 (4)
N1—C1—C5	114·2 (4)	N3—C9—C10	117·1 (4)
C2—C1—C8	110·6 (4)	N3—C9—C12	118·4 (4)
C2—C1—C5	102·1 (4)	C2—C9—C10	104·1 (4)
C8—C1—C5	103·0 (4)	C2—C9—C12	109·4 (4)
C3—C2—C9	103·4 (4)	C10—C9—C12	89·8 (4)
C3—C2—C1	104·9 (4)	C4—C10—C11	109·0 (5)
C9—C2—C1	99·1 (4)	C4—C10—C9	102·3 (4)
C4—C3—C2	94·8 (4)	C11—C10—C9	90·3 (5)
C3—C4—C10	104·6 (4)	C6—C11—C10	109·3 (5)
C3—C4—C5	104·3 (5)	C6—C11—C12	102·5 (5)
C10—C4—C5	99·5 (4)	C10—C11—C12	90·2 (4)
N2—C5—C4	113·5 (5)	C8—C12—C11	103·9 (4)
N2—C5—C6	112·4 (5)	C8—C12—C9	107·9 (4)
N2—C5—C1	114·2 (5)	C11—C12—C9	89·7 (4)

O1—N1—C1—C2	127·7 (6)	O4—N2—C5—C6	127·4 (8)
O1—N1—C1—C8	1·1 (8)	O4—N2—C5—C1	−117·0 (7)
O1—N1—C1—C5	−116·9 (7)	O5—N3—C9—C2	−176·3 (5)
O2—N1—C1—C2	−53·9 (7)	O5—N3—C9—C10	61·2 (7)
O2—N1—C1—C8	179·6 (6)	O5—N3—C9—C12	−44·6 (7)
O2—N1—C1—C5	61·5 (7)	O6—N3—C9—C2	5·1 (6)
O3—N2—C5—C4	−179·4 (7)	O6—N3—C9—C10	−117·4 (5)
O3—N2—C5—C6	−52·8 (9)	O6—N3—C9—C12	136·8 (5)
O3—N2—C5—C1	62·8 (9)	N1—C1—C5—N2	2·1 (6)
O4—N2—C5—C4	8 (9)		

Table 3. *Comparison of bishomopentaprismane* C—C *bond lengths* (Å)



(V): $X = \mathrm{CHNO_2}$, $Z = \mathrm{C(NO_2)_2}$
(VI): $X = Z = \mathrm{C(NO_2)_2}$
(VII): $X = Z = \mathrm{CHNO_2}$

Compound	C1—C5	Cyclobutane	Other
(IV)	1·578	1·549	1·533
(III)*	1·591	1·561	1·540
(V)	1·587	1·564	1·536
(VI)†	1·590	1·558	1·530
(VII)‡	1·563	1·545	1·534

* Two half molecules per asymmetric unit.
† Two molecules per asymmetric unit.
‡ One and a half molecules per asymmetric unit.

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* Lists of structure factors, anisotropic temperature factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54112 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bishomopentaprismane cage has approximate C_{2v} symmetry. The O—N—C1—C5 torsion angles would be ±90° in a molecule such as (III) with perfect C_{2v} symmetry. In (IV), the two nitro groups facing each other across C1—C5 show appreciable N1—C1 and N2—C5 torsion-angle deviations from 90° with (O1,O2)—N1—C1—C5 and (O4,O3)—N2—C5—C1 dihedral angles of −117·4, 62·0° and −117·3, 63·3°, respectively. The nitro groups in one of the two crystallographically distinct molecules (*A*) of (III) show similar torsion angles of −124·5, 57·2° while in the other molecule (*B*) the nitro groups are closer to the C_{2v} relationship with −99·2, 79·5°. The nitro N···N and O···O distances in (IV) and (III*B*) are similar at 2·80, 3·29 Å and 2·82, 3·32 Å whereas in (III*A*) the values are 2·74, 3·16 Å. This similarity extends to the N—C—C angles of 114·1° in (IV) and 114·0° in (III*B*), but 112·4° in (III*A*).

A partial crystal packing diagram for (IV) is shown in Fig. 2. All C—H distances were normalized to 1·10 Å and the H···O distances less than 2·6 Å are illustrated. With the exception of a 2·26 Å distance from O5···H4 (molecule at $\frac{1}{2}+x$, $\frac{3}{2}-y$, z), the H···O intermolecular distances are equal to or greater than the typical van der Waals distance of 2·5–2·6 Å. The 2·26 Å distance, which results from the protruding basal nitro group, is presumably counteracted by numerous weak attractive interactions between the molecules. A 2·5–2·6 Å distance presumably would result in a substantially larger crystal lattice energy and lower density.

A number of density-related parameters together with the percent changes encountered from unsubstituted (I) and (III) to basal-nitro-substituted (II) and (IV) are listed in Table 4. The changes in molecular volume, total surface area, accessible surface area and molecular density are normal for the replacement of H in (I) and (III) by NO_2. The percent changes in many of these quantities from (III) to (IV) would be expected to be smaller than from (I) to (II) simply because (III) is larger than (I). The most striking differences between the (I)/(II) and (III)/(IV) pairs are found in the crystal densities (ρ_x) and packing coefficients (PC's). In (I)/(II), the increase in ρ_x parallels ρ_{mol} and there is effectively no change in the PC whereas in (III)/(IV) the ρ_x's differ by about 0·04 g cm^{-3} and the PC's decrease by about 4%. Ordinarily, an increase in ρ_{mol} would produce a concomitant change in ρ_x, but in the case of (III)/(IV) the ρ_{mol} increase is opposed by the decrease in PC.

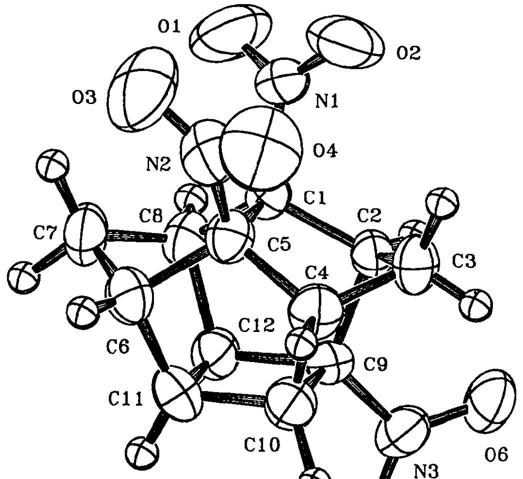

Fig. 1: *ORTEP* drawing of (IV). The C, O and N atoms are shown as 45% ellipsoids, and the H atoms are depicted as spheres with $B = 1{\cdot}5$ Å^2.

The 0·733 PC of (III) is anomalously high in comparison to the 0·703–0·716 values for (I), (II) and (IV), indicating more efficient crystal packing for (III) than for other molecules of this type. The crystal structure of (III) contains two half molecules per asymmetric unit, each arranged about a twofold axis in *P*2/*c* (see Fig. 3). There are no intermolecular

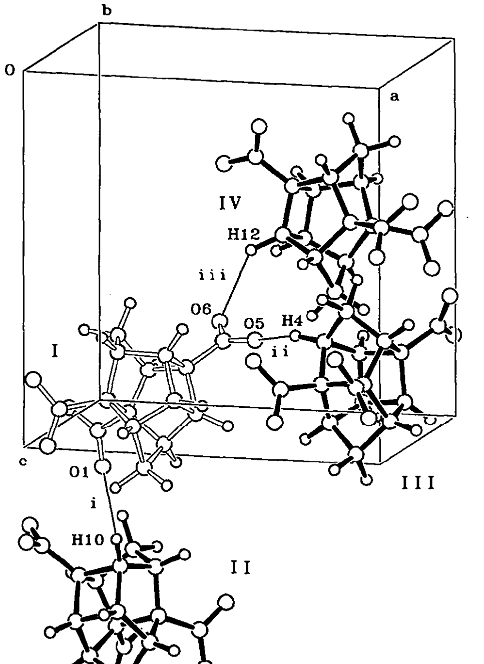

Fig. 2. *ORTEP* packing drawing for (IV) with O···H intermolecular distances < 2·6 Å shown. C—H bonds have been normalized to 1·10 Å. The Roman numerals refer to molecules at the following symmetry locations: (I) x, y, z; (II) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}+z$; (III) $\frac{1}{2}+x, \frac{3}{2}-y, z$; (IV) $1-x, 1-y, -\frac{1}{2}+z$. The intermolecular distances indicated are: (i) = 2·55; (ii) = 2·26; (iii) = 2·55 Å.

Table 4. *Comparison of several density-related parameters for* (I)–(IV)

Parameters calculated with *SVDHA* (Zhang, 1985). All C—H lengths were normalized to 1·10 Å. van der Waals radii used are C = 1·70, H = 1·1, N = 1·55, O = 1·52 Å. % change = {parameter [(II) or (IV)] − parameter [(I) or (III)]}/parameter [(I) or (III)].

	(I)*	(II)†‡	% change (I) to (II)	(III)†	(IV)	% change (III) to (IV)
Molecular weight	188·2	233·2	23·9	248·2	293·2	18·1
Molecular volume (Å^3)	158·3	181·2	14·5	190·2	210·6	10·7
Molecular surface area (Å^2)	181·2	210·2	16·0	217·2	241·9	11·4
Accessible surface area (Å^2)¶	71·5	82·8	15·9	80·6	94·3	17·0
Molecular density (g cm^{-3})	1·975	2·136	8·2	2·167	2·312	6·7
Crystal density from unit-cell volume (g cm^{-3})	1·415	1·521	7·5	1·589§	1·625	2·3
Packing coefficient**	0·716	0·712	~0	0·733§	0·703	−4·1

* Crystal structure reference: Engel, Fischer & Paquette (1984).

† Values given for (II) and (III) are averages for the two molecules per asymmetric unit.

‡ Crystal structure reference: Ammon & Paquette (1991).

§ The crystal structure of (III) was determined at 133 K. These data were calculated from the unit-cell dimensions reported at 296 K (Paquette, Fischer & Engel, 1985).

¶ Surace area of a molecule that can be in contact with an external atom with a radius of 1·52 Å.

** Molecular volume/unit-cell volume per molecule.

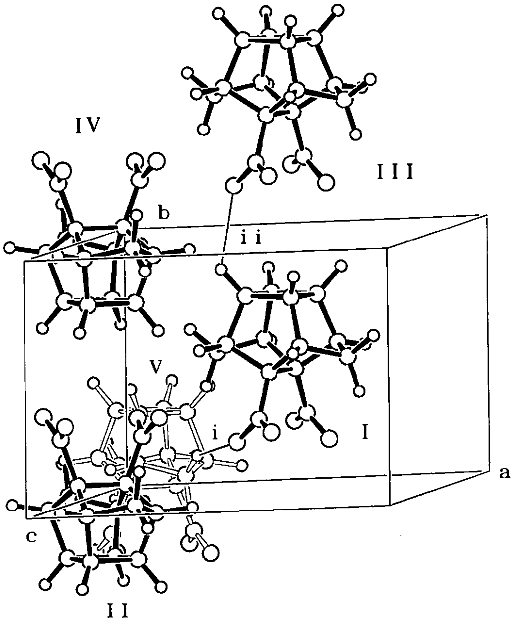

Fig. 3. Partial crystal packing diagram for (III) with O···H intermolecular distances < 2·6 Å shown. C—H bonds have been normalized to 1·10 Å. The unit-cell origin is hidden by molecule (I). The Roman numerals refer to the following: (I) = (III*A*) molecule at *x*, *y*, *z*; (II) = (III*B*) molecule at *x*, *y*, *z*; (III) = *A* at *x*, 1 + *y*, *z*; (IV) = *B* at *x*, 1 + *y*, *z*; (V) = *A* at *x*, −*y*, $-\frac{1}{2}+z$. The intermolecular distances indicated are: (i) = 2·51; (ii) = 2·56 Å.

O···H distances less than 2·5 Å [again, it should be emphasized that the crystal structure determination of (III) was at 133 K]. The unit translation symmetry operation along the relatively short *b* axis nestles the negatively charged NO_2-containing top of one molecule against the positively charged C—H-containing bottom of another. The molecules are shaped somewhat like cylinders (the top is actually ellipsoid shaped), which permits efficient side-to-side packing, and the −top/+bottom polarity allows efficient cylinder stacking along **b**. Additionally, the two unique molecules per asymmetric unit have opposite orientations and are positioned along the twofold axes to optimize side-to-side hydrophobic interactions between adjacent bishomopentaprismane cages.

In summary, the proposal (Shen & Paquette, 1989) that basal-nitro substitution in selected [4]peristylanes and a bishomopentaprismane may not lead necessarily to higher crystal densities has been investigated. It has been shown that crystal packing and density of nitro-substituted (IV) are normal and that the somewhat higher crystal packing efficiency in (III) is the result of molecular shape and polarity. It is suggested that the absence of the typical crystal-density increase with basal-nitro substitution will be observed only in those systems in which the unsubstituted precusor has higher-than-normal crystal packing efficiency.

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Structure of Ammonium Hydrogen Bis(phosphoenolpyruvate)

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Abstract. Ammonium hydrogen bis[2-(phosphonooxy)propenoate], $NH_4^+.C_3H_4O_6P^-.C_3H_5O_6P$, $M_r = 353·12$, monoclinic, $P2_1$, $a = 7·618\,(4)$, $b = 22·321\,(10)$, $c = 8·311\,(3)$ Å, $\beta = 90·14\,(4)°$, $V = 1413·2\,(11)$ Å^3, $Z = 4$, $D_m = 1·668$, $D_x = 1·660\,(2)$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 3·78$ cm^{-1}, $F(000) = 728$, $T = 298\,(2)$ K, final $R = 0·0354$ for 4625 observed reflections. The asymmetric unit contains two phosphoenolpyruvic acid molecules, two phosphoenolpyruvate monoanions and two ammonium cations. The P—O$_{\rm ester}$ bond lengths are 1·590 (3) and 1·594 (3) Å in the acid molecules and 1·614 (2) and 1·609 (2) Å in the monoanions. All OH and NH groups are involved in intermolecular hydrogen bonds.

Introduction. This investigation was undertaken as part of a study of the structure of the phosphoenolpyruvate (PEP) moiety which may exist in four different forms: the tribasic acid, monoanion, dianion and trianion. All these forms have been characterized in the crystalline state (Weichsel & Lis, 1991). Recently, we prepared new PEP salts by saturating aqueous or alcoholic solutions of PEP acid with gaseous ammonia. This procedure usually produces monoammonium and triammonium salts (Weichsel & Lis, 1991). Here we report the structure of an acid ammonium PEP salt of formula NH_4^+.PEP$^-$.PEP which can also be obtained by this procedure.

Experimental. Almost parallelepipedal platy crystals of the title compound were obtained at ~277 K by slow concentration of an aqueous solution of PEP acid (Weichsel, Lis & Kuczek, 1989) and ammonium hydroxide in a molar ratio of 5:1. Slightly higher ammonium concentrations (*e.g.* a molar ratio of 3:1) result in orthorhombic crystals of the monoammonium PEP salt (Weichsel & Lis, 1991). The crystals were grown also by extremely slow diffusion of ammonia through the vapour phase into concentrated solution of PEP acid at ~277 K. The density of the crystals was measured by flotation in $CHCl_3$/$C_2H_4Br_2$; preliminary examination by oscillation and Weissenberg photographs. A fragment (0·35 × 0·25 × 0·5 mm) was cut from a larger crystal and covered with protective lacquer. A Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation and graphite monochromator were used for measurements of lattice parameters (15 reflections in the range $20 < 2\theta < 25°$) and intensities. An almost full Ewald sphere up to $2\theta = 56°$ was collected operating in the ω–2θ scan mode. After each group of 50 reflections two standards were measured, variation ± 8%. The intensities were corrected for Lorentz and polarization factors only. Of 7918 measured reflections 6589 had $I > 3\sigma(I)$. Merging these in point group 2 yielded 4625 reflections with h −10–10, k −29–29, l −10–10 (including 2187 Friedel pairs) which were used for the structure analysis; $R_{\rm merge}$ was 0·0287.

The structure was solved by the use of direct methods (Sheldrick, 1986). Refinement was by full-matrix least-squares methods (Sheldrick, 1976), minimizing the function $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F_o)$, where $\sigma(F_o)$ was based on counting statistics. The H atoms were found from difference Fou-

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