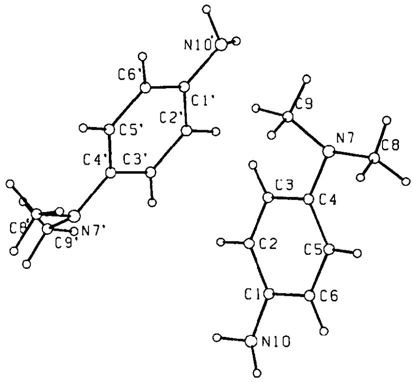

Fig. 1. Perspective view with the atom-labeling system for *N*,*N*-dimethyl-1,4-phenylenediamine. The atom labels are primed for molecule *B*.

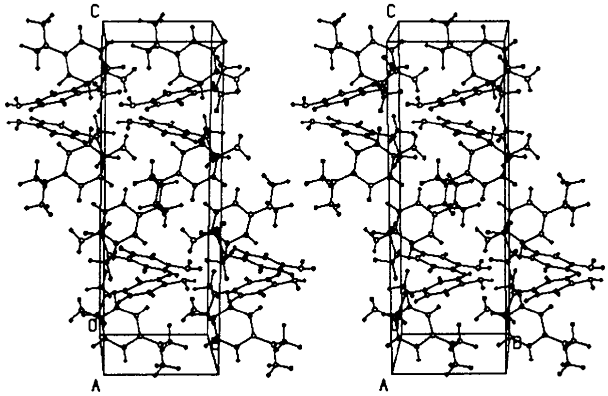

Fig. 2. A stereoview of the unit-cell packing.

the extension of the bond C(*ipso*)–N (Christen, Norbury, Lister & Palmieri, 1975). The values of φ(dimethylamino) and φ(amino) are respectively 41·7 and 48·2° for molecule *A*, and 42·2 and 45·0° for molecule *B*. The corresponding values in the complex with 1,2,4,5-tetracyanobenzene are 29·0 and 25·3°. Thus, the planarities of the amino and the dimethylamino groups increase on complex formation. One of the most probable reasons for this is the disappearance of hydrogen bonds to the lone-pair electrons on the N atoms. In comparison with the complex, bond lengthening was observed in the molecular structures; C(2)–C(3), C(5)–C(6) and C(4)–N(7) are longer than 1·358 (7), 1·376 (7) and 1·412 (6) Å in the complex, respectively. Thus, the contribution of a quinoidal form to the molecular structure is less than that in the complex. This finding supports the decrease in conjugation between the phenyl ring and the dimethylamino group resulting from the increase in the non-planarity of the group. In addition, this increase would lead to a decrease of hyperconjugation between the methyl groups and the lone-pair orbital on the N atom. In fact, the N–Me bond distances are longer than 1·445 (7) and 1·441 (8) Å in the complex.

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Structure of the Quasi-equatorial Isomer of 5,11-Dinitrohexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{4,8}.0^{9,12}]dodecane and Crystal Density Calculations for Several Di-, Tri- and Tetranitro Analogs

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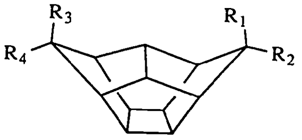
Abstract. $C_{12}H_{12}N_2O_4$, $M_r = 248{\cdot}24$, monoclinic, $C2/c$, $a = 25{\cdot}448$ (2), $b = 9{\cdot}165$ (1), $c = 17{\cdot}248$ (5) Å, $\beta = 127{\cdot}35$ (2)°, $V = 3198$ (1) Å^3, $D_x = 1{\cdot}547$ g cm^{-3} for $Z = 12$, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}3$ cm^{-1}, $F(000) = 1560$ e, $T = 294$ K, diffractometer data, 2927 unique data, 1440 $I > 3\sigma(I)$, $R = 0{\cdot}045$. Eight molecules are in general positions; four are in special positions on the crystallographic dyads. Each molecule contains one four-membered and six five-membered rings and has a basket-like shape. The two nitro substituents occupy positions that are slightly below the rim of the basket. The average C—C—C angles in the four- and five-membered rings are 90·0 (3) and 103·2 (4)°, respectively; the C—C bonds range from 1·509 (6) to 1·576 (6) Å, with an average of 1·551 (6) Å. The densities calculated for several di-, tri- and tetranitro analogs are compared with experimental values previously reported in the literature.

Introduction. For the past few years, Dr D. T. Cromer and others at the Los Alamos Scientific Laboratory (LASL), Dr J. R. Holden at the Naval Surface Weapons Center in Silver Spring, MD, and this laboratory have been collaborating on the development of a method for the prediction (calculation) of the crystal densities of energetic materials. The goal is an accuracy of 2% or better. The overall procedure that evolved and continues to be refined contains three major steps: (1) construct a reasonable three-dimensional model for the compound of interest; (2) molecular packing search to identify several possible 'crystal structures'; (3) lattice-energy refinement of the several structures. It is assumed that the structure corresponding to the lowest lattice energy is the best one, and a simple calculation gives the crystal density from the structure. The LASL efforts have been primarily with step (3), Dr Holden has developed the step (2) procedures (*MOLPAK* program and others) and this laboratory has been mainly involved with steps (1) and (3). The *WMIN* program (Busing, 1981) is used exclusively for step (3), and considerable efforts have been expended at LASL and in this laboratory to develop force-field coefficients capable of giving accurate densities for C,H,N,O-containing energetic compounds.

We are continually on the look-out for interesting structures to serve as test cases for density prediction. Dr A. Marchand of North Texas State University had suggested that we investigate the compounds reported in a paper by Paquette, Nakamura & Engel (1986). This publication described the synthesis of several nitro-1,3-bishomopentaprismanes, the crystal structures of two of the compounds were given and the densities for several, determined by solvent neutral buoyancy methods, were reported. Of particular interest to us for the purpose of testing the density prediction procedures was the substantial difference in densities reported for geometric isomers (II), 1·62 g cm^{-3}, and (III), 1·75 g cm^{-3}. Paquette *et al.* (1986) suggested that the higher density of (III) could be attributed to the pseudo-equatorial direction of the nitro substituents in (III) which permits more efficient molecular packing than the pseudo-axial nitro groups in (II).

In this paper, we report the crystal structure of (III), and the results of density calculations for (I)–(VI).



(I): $R_1 = R_4 = NO_2$
(II): $R_1 = R_3 = NO_2$
(III): $R_2 = R_4 = NO_2$
(IV): $R_1 = R_2 = R_4 = NO_2$
(V): $R_1 = R_2 = R_3 = NO_2$
(VI): $R_1 = R_2 = R_3 = R_4 = NO_2$

Experimental. *Structure determination of* (III). Colorless somewhat opaque crystals were obtained from Dr L. A. Paquette, 0·13 × 0·26 × 0·46 mm prism, Enraf–Nonius CAD-4 diffractometer, Mo radiation with incident-beam graphite monochromator, cell parameters from 25 reflections automatically centered in the range $6·6 < \theta < 16·4°$, 2θ–θ scan at variable θ speed of 8·24–1·50° min^{-1}, θ scan range = 1·5° + 0·34°tanθ, peak obtained from the central 2/3 of the overall scan, backgrounds from the two outer 1/6 regions of the scan, θ range for data collection of 1·5–25°, index range of $h = 0$–24, $k = 0$–10, $l = \overline{16}$–16, 7 standards measured at 300-reflection intervals, av. and max. standard intensity variations of 0·9 and 3·7%, 3004 total data measured (includes the $h0l$, l odd reflections), 2927 unique data, 1440 $I > 3\sigma(I)$. All crystallographic calculations were performed with the *TEXSAN* (1986) program system on a DEC MicroVax II computer. Structure solved with the *MITHRIL* direct-methods link, refinement by full-matrix least squares with anisotropic temperature factors for C, N and O and isotropic terms for H (H atoms were initially positioned from the C-framework geometry), minimization of $\sum w(F_o - F_c)^2$, $w = 1/\sigma(F_o)$, secondary-extinction parameter refined, final S, R and wR values of 1·69, 0·046, 0·053, max. shift/e.s.d. of 0·028, min. and max. values in the final difference map of −0·172 and 0·179 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Atomic coordinates are listed in Table 1.*

Density calculations for (I)–(VI). Molecular models for these compounds were obtained either from the known crystal structures or by appropriate modifications of known structures. A model of (I), for example, was created from the crystal structure coordinates of (V) by replacing the R_2 nitro substituent with an H atom, followed by the adjustment of all C—H lengths to 1·1 Å. These manipulations were performed with the *CHEMGRAF* (1984) computer-graphics program on a Lundy S5688 graphics terminal.

The next step utilizes the molecular model and the program *MOLPAK* (Holden, 1987) to generate a

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Center as Supplementary Publication No. SUP 44756 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and* B_{eq} *values for* (III)

$$B_{\mathrm{eq}} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
O1	0·2084 (2)	0·4074 (4)	−0·1027 (2)	6·9 (2)
O2	0·2861 (2)	0·5618 (4)	−0·0117 (3)	7·8 (2)
O3	0·0478 (2)	0·4493 (5)	0·1921 (3)	8·8 (2)
O4	0·1388 (2)	0·3352 (4)	0·2595 (2)	7·2 (2)
O5	0·3799 (2)	0·4634 (4)	0·3478 (3)	8·3 (2)
O6	0·4730 (2)	0·3542 (3)	0·4442 (2)	6·8 (2)
N1	0·2322 (2)	0·5088 (4)	−0·0448 (3)	5·6 (2)
N2	0·0995 (2)	0·4289 (4)	0·2046 (3)	5·6 (2)
N3	0·4367 (2)	0·4408 (4)	0·3791 (3)	5·6 (2)
C1	0·1925 (2)	0·5741 (5)	−0·0156 (3)	4·8 (2)
C2	0·2302 (2)	0·5705 (5)	0·0949 (3)	5·0 (2)
C3	0·1775 (2)	0·6238 (5)	0·1048 (3)	4·6 (2)
C4	0·1856 (2)	0·5369 (5)	0·1878 (3)	5·0 (2)
C5	0·1137 (2)	0·5215 (5)	0·1478 (3)	5·1 (2)
C6	0·0899 (2)	0·4479 (5)	0·0513 (3)	4·7 (2)
C7	0·1114 (2)	0·5607 (5)	0·0107 (3)	4·8 (2)
C8	0·1342 (2)	0·4811 (4)	−0·0420 (3)	4·6 (2)
C9	0·2328 (2)	0·4078 (5)	0·1164 (3)	5·1 (2)
C10	0·2053 (2)	0·3873 (5)	0·1739 (3)	5·0 (2)
C11	0·1394 (2)	0·3265 (5)	0·0811 (3)	4·7 (2)
C12	0·1673 (2)	0·3473 (5)	0·0232 (3)	4·9 (2)
C13	0·4266 (2)	0·4888 (6)	0·2281 (3)	5·7 (2)
C14	0·4616 (2)	0·5287 (5)	0·3338 (3)	5·2 (2)
C15	0·5301 (2)	0·4879 (5)	0·3671 (3)	5·4 (2)
C16	0·5219 (2)	0·3362 (6)	0·3272 (4)	5·7 (2)
C17	0·4512 (2)	0·3364 (6)	0·2325 (3)	5·7 (2)
C18	0·4641 (2)	0·5784 (5)	0·2022 (3)	5·8 (2)
H1	0·179 (2)	0·672 (5)	−0·054 (3)	8 (1)
H2	0·272 (2)	0·621 (4)	0·134 (3)	6 (1)
H3	0·174 (2)	0·724 (4)	0·104 (3)	5 (1)
H4	0·216 (2)	0·576 (5)	0·250 (3)	8 (1)
H5	0·089 (2)	0·624 (4)	0·139 (2)	6 (1)
H6	0·042 (2)	0·423 (4)	0·008 (2)	4·3 (8)
H7	0·080 (2)	0·638 (4)	−0·026 (3)	6 (1)
H8	0·098 (2)	0·461 (4)	−0·118 (3)	7 (1)
H9	0·273 (2)	0·360 (4)	0·138 (3)	6 (1)
H10	0·226 (2)	0·331 (5)	0·231 (3)	8 (1)
H11	0·125 (2)	0·239 (4)	0·087 (3)	5 (1)
H12	0·170 (2)	0·265 (5)	−0·005 (3)	7 (1)
H13	0·384 (2)	0·498 (4)	0·189 (3)	5 (1)
H14	0·460 (2)	0·628 (4)	0·351 (3)	6 (1)
H15	0·564 (2)	0·498 (5)	0·436 (3)	7 (1)
H16	0·531 (2)	0·268 (6)	0·371 (3)	9 (2)
H17	0·420 (2)	0·264 (5)	0·221 (3)	8 (1)
H18	0·451 (2)	0·680 (5)	0·184 (3)	7 (1)

number of trial packing motifs or 'crystal structures'. The present version of *MOLPAK* can produce structures in triclinic space groups, monoclinic space groups with $Z = 2$ or 4 and orthorhombic space groups with $Z = 4$. The crystal structures with the smallest unit-cell volumes (most efficient packing) are selected for refinement by the *WMIN* program (see below) in the last step. It had been observed (Cromer, Ammon & Holden, 1987) that a *MOLPAK* search in space group $P\bar{1}$ followed by *WMIN* refinement gave crystal densities close to values obtained from a *WMIN* refinement in the correct space group for the compound of interest. In most cases, *MOLPAK* searches are limited to $P\bar{1}$ to conserve computer time.

The third and final step involves the refinement of the best of the *MOLPAK* structures with the *WMIN* program (Busing, 1981). The lattice energy, W, is computed as the sum of all atom-to-atom interactions between a molecule and surrounding molecules in the crystal:

$$W = [1/2Z]\sum\sum\{-A_iA_j/r_{ij}^6 + B_iB_j\exp[-(C_i+C_j)r_{ij}] + q_iq_j/r_{ij}\},$$

where the three terms represent van der Waals attraction, repulsion and Coulombic interactions. The A, B and C terms vary with atom type i, q is the atomic charge and r_{ij} is the distance between atoms i and j. Because the determination of realistic atomic charges is very computer-time intensive and would severely limit the utility of these procedures for routine density prediction, we opted to eliminate the Coulombic term and to use the energy-parameter-refinement features of *WMIN* together with crystal structure data for seventeen nitro-organics, to develop 'charge-less' A and B values for C, H, N and O. The C parameters were from the literature (Cox, Hsu & Williams, 1981; Williams & Weller, 1983); the A and B parameters used in this work ($A_{\mathrm{C}} = 38{\cdot}90$, $B_{\mathrm{C}} = 593{\cdot}4$, $A_{\mathrm{H}} = 13{\cdot}73$, $B_{\mathrm{H}} = 89{\cdot}0$, $A_{\mathrm{N}} = 42{\cdot}27$, $B_{\mathrm{N}} = 368{\cdot}3$, $A_{\mathrm{O}} = 59{\cdot}07$, $B_{\mathrm{O}} = 757{\cdot}1$ kJ$^{1/2}$ mol$^{-1/2}$ are a refinement of those given by Cromer *et al.* (1987). Structure refinement with *WMIN* involves minimization of the lattice energy as a function of structure parameters such as the unit-cell parameters, molecular orientation and position. The refined unit-cell parameters are used to calculate the crystal density (Table 3).

Discussion. Bond lengths and angles are listed in Table 2; an *ORTEP* drawing is given in Fig. 1. The molecule contains one four-membered and six five-membered rings and has a squarish basket-like shape. The four-membered ring forms the bottom of the basket, there are four five-membered rings at the four sides and two five-membered rings in the form of an eight-C-atom bicyclo[3.3.0]octane moiety constitute the top. The C—C bond that is common to both five-membered rings in the bicyclo[3.3.0]octane top can be thought of as the basket handle; the handle bonds, C3—C7 = 1·576 (6) and C18—C18′ = 1·550 (9) Å, are among the longest of the C—C bonds in the two molecules. The remainder of the C—C distances range from 1·509 (6) to 1·557 (6) Å and average 1·528 (6) Å. A similar pattern was observed in the tri- and tetranitro analogs; the corresponding basket-handle distances and remaining C—C averages are 1·588 (4) and 1·543 (4) Å in (V) and 1·591 (5) and 1·540 (6) Å in (VI) (Paquette *et al.*, 1986). In compounds such as cubane (Fleischer, 1964) and 1,4-dinitrocubane (Eaton, Shankar, Price, Pluth, Gilbert, Alster & Sandus, 1984), the average C—C distances are 1·551 (3) and 1·558 (3) Å. The four-membered ring C—C—C bond angles in (III) range from 89·5 (3) to 90·4 (3)°. In the five-membered rings, the C—C—C angles at the bridging atoms C1, C5 and C14 of 97·0 (3), 96·2 (3) and 95·6 (3)°, respectively, are substantially smaller than the other five-membered-ring C—C—C angles. This was also observed in (V) and (VI) (Paquette *et al.*, 1986).

The structural differences between the two independent molecules are associated with the C—NO_2 torsion angles. Alignment of the two C frameworks

Table 2. *Bond lengths* (Å), *angles* (°) *and e.s.d.'s* (*in parentheses*) *for* (III)

O1	N1	1·222 (4)	C6	C11	1·518 (5)
O2	N1	1·224 (4)	C6	C7	1·525 (5)
O3	N2	1·212 (5)	C7	C8	1·529 (5)
O4	N2	1·219 (4)	C8	C12	1·526 (5)
O5	N3	1·216 (4)	C9	C10	1·533 (6)
O6	N3	1·219 (4)	C9	C12	1·554 (6)
N1	C1	1·499 (5)	C10	C11	1·557 (6)
N2	C5	1·497 (5)	C11	C12	1·547 (6)
N3	C14	1·503 (5)	C13	C14	1·510 (6)
C1	C8	1·521 (6)	C13	C17	1·514 (7)
C1	C2	1·529 (6)	C13	C18	1·518 (6)
C2	C9	1·529 (6)	C14	C15	1·515 (6)
C2	C3	1·532 (6)	C15	C16	1·509 (6)
C3	C4	1·539 (6)	C15	C18	1·534 (6)
C3	C7	1·576 (6)	C16	C17	1·530 (6)
C4	C5	1·521 (6)	C16	C17*	1·546 (6)
C4	C10	1·528 (6)	C18	C18*	1·550 (9)
C5	C6	1·539 (5)			

O1	N1	O2	122·9 (4)	C12	C8	C7	100·6 (3)
O1	N1	C1	118·5 (4)	C2	C9	C10	107·9 (4)
O2	N1	C1	118·6 (4)	C2	C9	C12	103·7 (4)
O3	N2	O4	122·5 (4)	C10	C9	C12	90·1 (3)
O3	N2	C5	117·6 (4)	C4	C10	C9	108·2 (4)
O4	N2	C5	119·8 (4)	C4	C10	C11	103·4 (3)
O5	N3	O6	123·6 (4)	C9	C10	C11	90·4 (3)
O5	N3	C14	116·1 (4)	C6	C11	C12	107·7 (3)
O6	N3	C14	120·3 (4)	C6	C11	C10	103·9 (3)
N1	C1	C8	114·1 (3)	C12	C11	C10	89·5 (3)
N1	C1	C2	111·7 (4)	C8	C12	C11	108·1 (4)
C8	C1	C2	97·0 (3)	C8	C12	C9	104·0 (3)
C1	C2	C9	103·0 (3)	C11	C12	C9	90·0 (3)
C1	C2	C3	101·7 (4)	C14	C13	C17	103·9 (4)
C9	C2	C3	101·2 (4)	C14	C13	C18	102·1 (4)
C2	C3	C4	107·9 (4)	C17	C13	C18	101·5 (4)
C2	C3	C7	103·2 (3)	N3	C14	C13	111·8 (4)
C4	C3	C7	103·0 (3)	N3	C14	C15	114·9 (4)
C5	C4	C10	105·3 (3)	C13	C14	C15	95·6 (4)
C5	C4	C3	100·4 (3)	C16	C15	C14	104·2 (4)
C10	C4	C3	101·0 (3)	C16	C15	C18	101·2 (4)
N2	C5	C4	117·2 (4)	C14	C15	C18	101·7 (4)
N2	C5	C6	111·5 (3)	C15	C16	C17	103·5 (4)
C4	C5	C6	96·2 (3)	C15	C16	C17*	108·0 (4)
C11	C6	C7	101·3 (3)	C17	C16	C17*	89·9 (4)
C11	C6	C5	104·7 (3)	C13	C17	C16	103·7 (4)
C7	C6	C5	100·6 (3)	C13	C17	C16*	107·8 (4)
C6	C7	C8	108·7 (3)	C16	C17	C16*	90·1 (4)
C6	C7	C3	103·4 (3)	C13	C18	C15	108·2 (4)
C8	C7	C3	103·6 (3)	C13	C18	C18	103·4 (4)
C1	C8	C12	103·2 (3)	C15	C18	C18*	102·8 (4)
C1	C8	C7	102·0 (3)				

* Atom produced by the twofold symmetry operation.

shows that the two sets of C—NO_2 torsion angles differ by 7·3 (5)° at one end and 29·6 (5)° at the other end of the molecules.

The energy parameters given in the experimental section were used with *WMIN* to refine the reported structures (Paquette *et al.*, 1986) of (V) and (VI); densities calculated from the *WMIN*-refined structural parameters differed by 0·12 and −0·35%, respectively, from the experimental values (Table 3). Additionally, molecular models of (I)–(IV) were constructed by appropriate modifications of structure (VI), followed by *MOLPAK* searches for crystal packing arrangements primarily in space group $P\bar{1}$; in the case of (I), (II) and (IV), the best *MOLPAK–WMIN* $P\bar{1}$ structures gave densities that differed by −0·1 to +3·3% from literature values. The $P\bar{1}$ calculated density for (III) of 1·587 g cm^{-3} differed by 9·3% from the reported neutral buoyancy density value of 1·75 g cm^{-3}, and it was this discrepancy that prompted us to obtain crystals of the material from Dr Paquette for an X-ray structure determination. The X-ray density for (III) obtained in this crystallographic investigation is 1·547 g cm^{-3}; this new value, which is about 0·2 g cm^{-3} smaller than the solvent-derived density, differs from the $P\bar{1}$ value by a more reasonable −2·6%. It is likely that the solvent-derived densities reported for (II) and (IV) are also too high and we suggest that the $P\bar{1}$ calculated values are closer to the actual (presently unknown) crystal densities.

It should be underscored that *WMIN* refinement of a true crystal structure will give a lower lattice energy and higher density, in virtually all cases, than refinement of a hypothetical $P\bar{1}$ structure. We have found, however, that the $P\bar{1}$ densities are, in most cases, comparable to densities obtained from *WMIN* refinement of the actual crystal structure. The adoption of this $P\bar{1}$ short cut has been necessary to reduce the large amounts of computer time required for *MOLPAK* searches over a range of space-group possibilities. The last two lines of Table 3 illustrate one of the relatively rare instances in which a *MOLPAK*-derived non-$P\bar{1}$ space group produced a higher density than the $P\bar{1}$ result. *WMIN* refinement of the experimental crystal structure of (III) gave a density that differs by −1·75% from the experimental value.

With the new density value for (III), it can be seen that the pseudo-equatorial positions of the two nitro

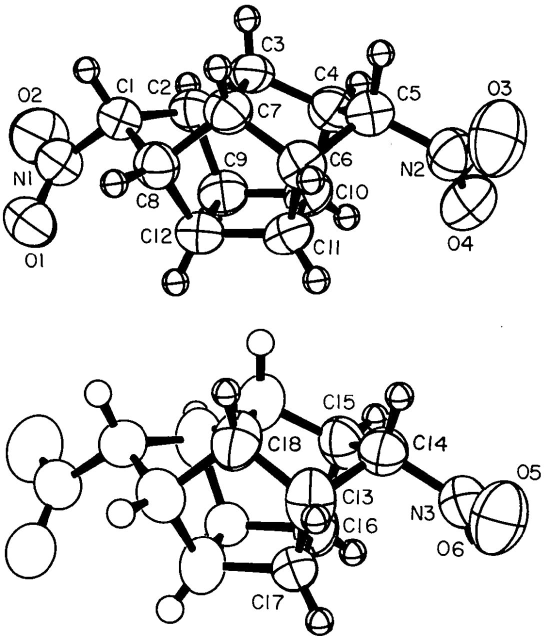

Fig. 1. *ORTEP* (Johnson, 1965) drawing of (III). The C, N and O atoms are shown as 50% ellipsoids, the H atoms as $B = 1·5$ Å^2 spheres. The unfilled atoms in molecule two are related to the filled atoms by the twofold symmetry.

Table 3. *Densities for* (I)–(VI)

	Experimental (g cm^{-3})	Space group (Z)	Calculated** (g cm^{-3})	Δ(%)‡
(I)	1·58*	$P\bar{1}$ (2)†	1·582	−0·13
(II)	1·62*	$P\bar{1}$ (2)†	1·567	3·27
(III)	1·547§††	$C2/c$(12)¶	1·574	−1·75
		$P\bar{1}$ (2)†	1·587	−2·58
(IV)	1·75*	$P\bar{1}$ (2)†	1·697	3·03
(V)	1·694‡‡	$P2_1/c$(4)¶	1·692	0·12
		$P\bar{1}$ (2)†	1·680	0·88
(VI)	1·739‡‡	$P\bar{1}$ (4)¶	1·745	−0·35
		$P\bar{1}$ (2)†	1·696	2·47
		$P2_1/c$ (4)†	1·724	0·87

* Determined by neutral buoyancy solvent methods (Paquette *et al.*, 1986).

† Space group (Z) used for *MOLPAK* search.

‡ $\Delta = [(\rho_{\rm exp} - \rho_{\rm calc})/\rho_{\rm exp}] \times 100$.

§ X-ray density calculated from unit-cell colume.

¶ Actual crystal space group; *MOLPAK* performed prior to *WMIN* calculations.

** Density obtained from a *WMIN* refinement of the structure in the indicated space group.

†† 1·75 g cm^{-3} reported previously, see * above.

‡‡ X-ray density calculated from unit-cell volume (Paquette *et al.*, 1986). The solvent-derived density of (VI) is 1·76 g cm^{-3}, see * above.

groups apparently do not increase packing efficiency by tucking the substituents under the basket rim as was previously suggested. That the calculated densities for the dinitro isomers (I)–(III) are within about 0·02 g cm^{-3} of each other indicates the crystal packing efficiencies are likely to be very similar and, therefore, are not influenced by the placement of the nitro-group substituents on the basket rim.

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Structure of 1-(4-Chlorobenzoyloxy)-4,5-dimethyl-1,2,3-triazole (CBODT)

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Abstract. 4,5-Dimethyl-1,2,3-triazolyl *p*-chlorobenzoate, $C_{11}H_{10}ClN_3O_2$, $M_r = 251{\cdot}67$, orthorhombic, $P2_12_12_1$, $a = 13{\cdot}675$ (2), $b = 11{\cdot}018$ (2), $c = 7{\cdot}990$ (1) Å, $V = 1203{\cdot}86$ Å^3, $Z = 4$, $D_m = 1{\cdot}398$, $D_x = 1{\cdot}388$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}17$ cm^{-1}, $F(000) = 520$, $T = 298$ K, final $R = 0{\cdot}057$ for 1176 unique reflections. The mean plane of the chlorophenyl ring is almost perpendicular [95·6 (2)°] to that of the triazole ring but is almost coplanar [7·3 (2)°] with that of the ester group. The latter forms an angle of 89·8 (2)° with the least-squares plane of the dimethyltriazole group.

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