Table 3. *Torsion angles* (°) *concerning the confor-mation of the seven-membered ring*

Endocyclic

χ_1	C(12)–N–C(8)–C(9)	62·1 (2)
χ_2	N–C(8)–C(9)–C(10)	−79·1 (2)
χ_3	C(8)–C(9)–C(10)–C(10')	65·4 (3)
χ_4	C(9)–C(10)–C(10')–C(11)	−1·2 (3)
χ_5	C(10)–C(10')–C(11)–C(12)	−63·4 (3)
χ_6	C(10')–C(11)–C(12)–N	81·2 (2)
χ_7	C(11)–C(12)–N–C(8)	−63·9 (2)

Exocyclic

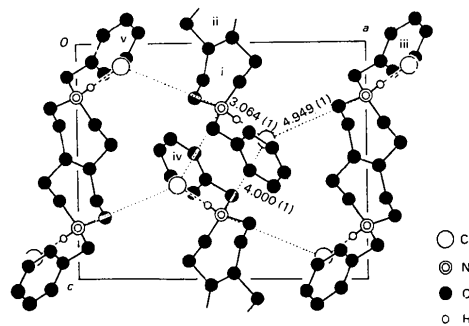|		
χ_8	C(9)–C(8)–N–C(7)	−174·0 (2)
χ_9	C(8)–N–C(7)–C(1)	169·8 (2)
χ_{10}	C(11)–C(12)–N–C(7)	173·6 (2)
χ_{11}	C(12)–N–C(7)–C(1)	−64·1 (2)
χ_{12}	N–C(7)–C(1)–C(2)	−84·6 (2)

Fig. 2. Molecular arrangement in a sheet parallel to (010). Interionic interactions are shown by dotted lines with the distances in Å. H atoms attached to C are omitted. Symmetry code: (i) x, y, z; (ii) $1-x, 1-y, -z$; (iii) $\frac{1}{2}+x, 1-y, \frac{1}{2}-z$; (iv) $1-x, 1-y, 1-z$; (v) $-\frac{1}{2}+x, 1-y, \frac{1}{2}-z$.

a chair-like conformation (Bocian & Strauss, 1977a,b) with a pseudo mirror plane passing through the N and the midpoint of the C(10)=C(10') bond. Such a conformation has recently been found in some cyclo-heptene rings (Weeks, Duax, Finnegan, Delecki & Kojić-Prodić, 1984).

The benzyl group is bonded equatorially to N: $\chi_8 = -174\cdot0$ (2)°. The exocyclic and endocyclic torsion angles in Table 3 are in agreement within 12° with the corresponding angles of the azacycloheptanone ring in 1-benzyl-5-phenyl-1-azacycloheptan-4-one hydro-chloride (Fukuyama, Shimizu, Kashino & Haisa, 1974). The endocyclic C—N and C(sp^3)—C(sp^2) bond lengths and bond angles are in agreement within the experimental errors with those found in the aza-cycloheptanone ring.

The molecular arrangement in a sheet parallel to (010) is shown in Fig. 2. It is seen that the sheet is formed by Coulombic interactions and hydrogen bonding, each ion being coordinated by three counter ions with N···Cl distances of 3·064 (1) (hydrogen bond), 4·000 (1) and 4·949 (1) Å. The short contacts in the sheet are: Cl···C(8^{iii}) 3·573 (2) and Cl···H(7^{iv}) 2·63 (2) Å. The sheets are stacked along **b** by van der Waals interactions.

The authors thank The Crystallographic Research Center, Institute for Protein Research, Osaka University, for the use of the facility.

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3,5-Diamino-2,4,6-trinitrobenzoic Acid, $C_7H_5N_5O_8$

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Abstract. $M_r = 287\cdot1$, monoclinic, $P2_1/c$, $a = 7\cdot2461$ (5), $b = 10\cdot3097$ (7), $c = 13\cdot962$ (1) Å, $\beta = 101\cdot023$ (6)°, $V = 1023\cdot8$ (2) Å^3, $Z = 4$, $D_x = 1\cdot862$ g cm^{-3}, $\lambda(\text{Cu } K\bar{\alpha}) = 1\cdot5418$ Å, $\mu = 15\cdot48$ cm^{-1}, $F(000) = 584$, $T = 294$ K, final $R = 0\cdot039$ for 1574 unique observed reflections. The results are compared

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with those of three analogs reported earlier with OH, F and $C(=O)NH_2$ substituents in place of COOH. The effects of amino and nitro substitution are exhibited by the benzene ring. Four of the six substituents of the benzene ring show substantial deviations from the ring plane. The carboxyl group, the two o-nitro groups and the p-nitro group are twisted out of the ring plane by 68·7 (3), 22·0 (3), 27·3 (3) and 14·6 (3)°, respectively. The amino groups are involved in both intra- and intermolecular contacts. The carboxyl group participates in the formation of a hydrogen-bonded dimer across a center of symmetry. The packing coefficients calculated for several 1-X-3,5-diamino-2,4,6-trinitrobenzenes suggest that crystal-packing efficiency is an important contribution to the high crystal densities of the compounds.

Introduction. Nitro-group substitutions in organic compounds invariably lead to an increase in the crystal density of the substituted compound. The present structure (I) relates to our continuing study on the relationship between structure and density of energetic substances. The structures of (II), (III) and (IV) (Bhattacharjee & Ammon, 1981; Ammon, Bhattacharjee & Holden, 1982; Ammon & Bhattacharjee, 1982), analogs of the present compound, have been reported previously.

(I) X = COOH
(II) X = OH
(III) X = F
(IV) X = C(=O)NH₂
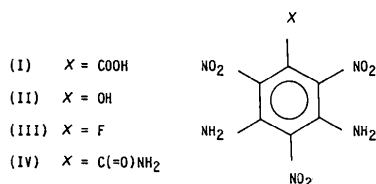
Experimental. Compound obtained from Drs H. Adolph and M. Chaykovsky, Naval Surface Weapons Center, Silver Spring, Maryland. Crystallized from 1-butanol as irregular polygons. Picker FACS-I diffractometer, graphite monochromator, Cu $K\bar{\alpha}$ radiation, 0·25 × 0·32 × 0·18 mm crystal, 2θ values of 12 reflections manually centered at $\pm 2\theta$ used to obtain accurate cell parameters by least squares (average $|2\theta_o - 2\theta_c|$ = 0·009°); θ–2θ scan, 2° min⁻¹, 10 s background, scan width (1·35 + 0·29 tanθ)°, four standards every 100 reflections with average and max. intensity deviations 2·24% and 3·20%, 1919 reflections measured, max. $2\theta = 126°$, 1648 unique reflections, 1574 of which were 3σ above background; max. and min. h, k, l 8, 11, 15 and 0, 0, −16; no correction for absorption; structure solved with direct-methods program *PHASE* in *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); full-matrix least-squares structure refinement, anisotropic temperature factors for C, N and O, individual isotropic terms for H (from ΔF map), $\sum w(F_o - F_c)^2$ minimized, $w = [1/\sigma(F)]^2$,

reflections with $I_c < 3\sigma(I)$ not included in refinement; max. and average shift/errors 0·314 [U_{23} of O(7)] and 0·087 in final l.s. cycle; max. and min. heights in final difference map 0·15 and −0·26 e Å⁻³; C, N and O scattering factors from Cromer & Mann (1968), H from Stewart, Davidson & Simpson (1965), final $R = 0·039$, $wR = 0·042$ and $S = 2·97$. Univac 1100/82 computer at the University of Maryland's Computer Science Center, *XRAY*76 system of crystallographic programs (Stewart *et al.*, 1976).

Table 1. *Fractional coordinates and isotropic temperature factors* (Å²)

An asterisk denotes U_{eq}, the equivalent value of the anisotropic temperature-factor coefficients, calculated from the expression: $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. The U_{ij} values have been deposited. The e.s.d. of the last significant digit is given in parentheses.

|	x	y	z	U_{eq}/U_{iso}
C(1)	0·5846 (3)	0·3473 (2)	0·4261 (1)	0·022 (3)*
C(2)	0·4550 (3)	0·3885 (2)	0·3459 (1)	0·026 (4)*
C(3)	0·2823 (3)	0·3192 (2)	0·3126 (1)	0·024 (4)*
C(4)	0·2431 (3)	0·2149 (2)	0·3727 (1)	0·021 (4)*
C(5)	0·3636 (3)	0·1815 (2)	0·4627 (1)	0·028 (4)*
C(6)	0·5427 (3)	0·2449 (2)	0·4819 (1)	0·025 (4)*
C(7)	0·7689 (3)	0·4187 (2)	0·4573 (2)	0·026 (4)*
N(1)	0·4915 (2)	0·5099 (2)	0·3009 (1)	0·033 (5)*
N(2)	0·1627 (3)	0·3572 (2)	0·2340 (1)	0·031 (5)*
N(3)	0·0718 (2)	0·1427 (2)	0·3430 (1)	0·025 (5)*
N(4)	0·3189 (3)	0·0941 (2)	0·5242 (2)	0·042 (3)*
N(5)	0·6884 (3)	0·2003 (2)	0·5611 (1)	0·031 (3)*
O(1)	0·7957 (2)	0·4815 (2)	0·5332 (1)	0·023 (3)*
O(2)	0·8862 (2)	0·4032 (2)	0·3991 (1)	0·029 (5)*
O(3)	0·6004 (3)	0·5863 (2)	0·3493 (1)	0·033 (3)*
O(4)	0·4120 (2)	0·5356 (2)	0·2168 (1)	0·044 (2)*
O(5)	−0·0152 (3)	0·1508 (2)	0·2587 (1)	0·028 (2)*
O(6)	0·0140 (2)	0·0701 (2)	0·4015 (1)	0·038 (5)*
O(7)	0·6468 (3)	0·1459 (2)	0·6325 (1)	0·058 (2)*
O(8)	0·8523 (2)	0·2171 (2)	0·5534 (1)	0·048 (1)*
H(2A)	0·184 (4)	0·433 (3)	0·204 (2)	0·051 (7)
H(2B)	0·068 (4)	0·305 (3)	0·216 (2)	0·063 (9)
H(4A)	0·395 (4)	0·084 (3)	0·579 (2)	0·065 (9)
H(4B)	0·197 (4)	0·058 (3)	0·506 (2)	0·073 (9)
H(O2)	1·000 (6)	0·454 (4)	0·422 (3)	0·12 (1)
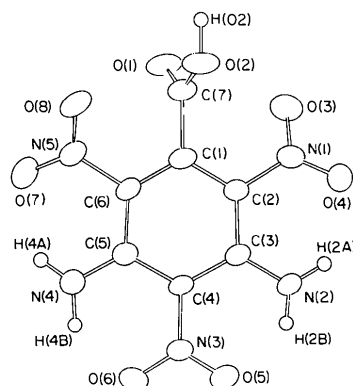
Fig. 1. An *ORTEP*II drawing of (I) with the C, N, and O atoms depicted as 50% probability boundary ellipses. H atoms are shown as 0·1 Å radius circles.

Discussion. Atomic coordinates and isotropic thermal parameters are listed in Table 1.*

An *ORTEP*II (Johnson, 1976) drawing of the molecule is shown in Fig. 1. The maximum and average deviations of the six ring atoms from their least-squares plane are 0·067 (4) and 0·040 (5) Å. Four of the six ring substituents deviate substantially from the plane [N(1) = 0·321, N(2) = 0·001, N(3) = −0·107, N(4) = 0·204, N(5) = −0·209, C(7) = 0·011 Å]; the pattern of the out-of-plane deviations is one which reduces intramolecular crowding.

Bond lengths, angles and torsion angles are listed in Table 2. Bond lengths and angles in the aromatic rings of (I)–(IV) show the effects of the amino and nitro substituents (Holden & Dickinson, 1977). For example, the four benzene C—C bonds per molecule directly associated with the amino-group fragments [*i.e.* C—C(NH$_2$)—C] are substantially longer than the usual 1·40 Å value observed in ordinary aromatic rings: the four C—C bond-length averages in (I)–(IV) are 1·431 (3), 1·434 (9), 1·433 (7) and 1·434 (3) Å, respectively. The averages of the internal C—C—C angles at the benzene-ring atoms linked to the amino [*i.e.* C—C(NH$_2$)—C] and the nitro [*i.e.* C—C(NO$_2$)—C] substituents are 116·0 (2) and 122·2 (2)°, 116·5 (6) and 121·4 (6)°, 116·4 (4) and 122·1 (4)° and 116·2 (2) and 122·2 (2)° in (I)–(IV).

The eight C—NH$_2$ distances in the four compounds are remarkably similar, ranging from 1·314 (7)–1·332 (3) Å with an average of 1·321 (8) Å. The twelve C—NO$_2$ distances cover the wider range of 1·409 (6)–1·463 (6) Å [average 1·439 (9) Å] although the four C(4)—N bonds span the more limited range of 1·420 (3)–1·439 (2) Å [average 1·428 (7) Å]. These similarities and differences may be attributed, at least in part, to variations in the C—N twist angles. The C(4)—NO$_2$ angles cover the relatively narrow range of 4·5 (3)–17·8 (8)° whereas the range is 3·4 (8)–54·5 (4)° for the C(6)—NO$_2$ and C(2)—NO$_2$ angles. In (I), the C—NO$_2$ twist angles at C(2), C(4) and C(6) are 22·0 (3), 14·6 (3) and 27·3 (3)°, respectively. The C(1)—CO$_2$H twist angle is 68·7 (3)°, similar to the C—C(=O)NH$_2$ angle in (IV) of 70·0 (3)°. The corresponding C(1)—C(7) distances in (I) and (IV) are 1·514 (3) and 1·530 (3) Å. A comparison of the twelve-atom central cores (aromatic ring plus the six ring substituent atoms) in (I) and (IV) with Nyburg's (1974) molecule-fitting program gave an r.m.s. deviation of 0·066 Å.

A packing diagram is shown in Fig. 2. The pattern of strong intramolecular N—H···O interactions between adjacent NH$_2$ and NO$_2$ groups observed in (II)–(IV) is

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42036 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

repeated here; the range of H···O distances is 1·78 (3)–1·94 (3) Å. The strongest intermolecular interaction is due to the formation of a hydrogen-bonded carboxylic acid dimer across a center of symmetry; the O(2)—H(O2)···O(1) (at 2−*x*, 1−*y*, 1−*z*) and O(2)···O(1) distances are 1·64 (4) and 2·605 (2) Å respectively. Two of the four amino hydrogen atoms participate in

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

C(1)—C(2)	1·385 (3)	C(5)—N(4)	1·327 (3)
C(1)—C(6)	1·379 (3)	C(6)—N(5)	1·451 (3)
C(1)—C(7)	1·514 (3)	C(7)—O(1)	1·226 (3)
C(2)—C(3)	1·438 (3)	C(7)—O(2)	1·294 (3)
C(2)—N(1)	1·447 (3)	N(1)—O(3)	1·223 (2)
C(3)—C(4)	1·426 (3)	N(1)—O(4)	1·234 (2)
C(3)—N(2)	1·321 (3)	N(3)—O(5)	1·226 (2)
C(4)—C(5)	1·428 (3)	N(3)—O(6)	1·239 (3)
C(4)—N(3)	1·439 (2)	N(5)—O(7)	1·231 (3)
C(5)—C(6)	1·431 (3)	N(5)—O(8)	1·225 (3)

C(2)—C(1)—C(6)	120·2 (2)	C(1)—C(6)—C(5)	122·2 (2)
C(2)—C(1)—C(7)	120·5 (2)	C(1)—C(6)—N(5)	117·8 (2)
C(6)—C(1)—C(7)	119·2 (2)	C(5)—C(6)—N(5)	120·0 (2)
C(1)—C(2)—C(3)	121·5 (2)	C(1)—C(7)—O(1)	119·4 (2)
C(1)—C(2)—N(1)	117·7 (2)	C(1)—C(7)—O(2)	114·1 (2)
C(3)—C(2)—N(1)	120·6 (2)	O(1)—C(7)—O(2)	126·5 (2)
C(2)—C(3)—C(4)	116·3 (2)	C(2)—N(1)—O(3)	118·0 (2)
C(2)—C(3)—N(2)	120·9 (2)	C(2)—N(1)—O(4)	120·5 (2)
C(4)—C(3)—N(2)	122·7 (2)	O(3)—N(1)—O(4)	121·5 (2)
C(3)—C(4)—C(5)	122·8 (2)	C(4)—N(3)—O(5)	119·9 (2)
C(3)—C(4)—N(3)	118·6 (2)	C(4)—N(3)—O(6)	120·3 (2)
C(5)—C(4)—N(3)	118·5 (2)	O(5)—N(3)—O(6)	119·8 (2)
C(4)—C(5)—C(6)	115·7 (2)	C(6)—N(5)—O(7)	120·5 (2)
C(4)—C(5)—N(4)	123·3 (2)	C(6)—N(5)—O(8)	117·7 (2)
C(6)—C(5)—N(4)	120·9 (2)	O(7)—N(5)—O(8)	121·8 (2)

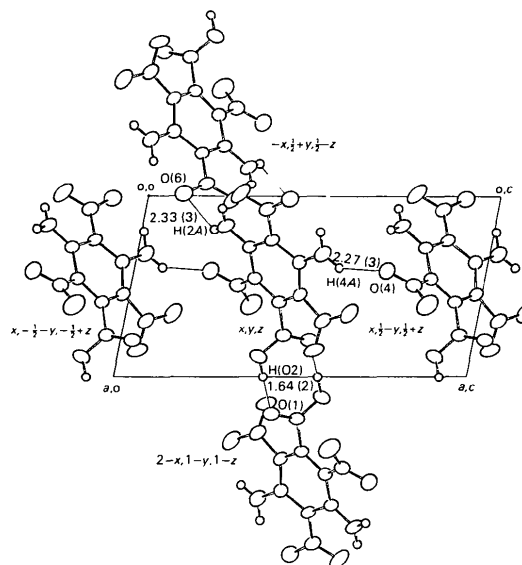|			
C(1)—C(2)—N(1)—O(3)	−20·1 (3)	C(3)—C(2)—N(1)—O(3)	155·0 (2)
C(1)—C(2)—N(1)—O(4)	161·1 (2)	C(3)—C(2)—N(1)—O(4)	−23·8 (3)
C(1)—C(6)—N(5)—O(7)	153·8 (2)	C(3)—C(4)—N(3)—O(5)	16·4 (3)
C(1)—C(6)—N(5)—O(8)	−27·3 (3)	C(3)—C(4)—N(3)—O(6)	−165·3 (2)
C(2)—C(1)—C(7)—O(2)	−71·2 (3)	C(5)—C(4)—N(3)—O(5)	−165·6 (2)
C(2)—C(1)—C(7)—O(1)	110·2 (2)	C(5)—C(4)—N(3)—O(6)	12·8 (3)

Fig. 2. Packing view down **b**; intermolecular contact distances (Å) with e.s.d.'s in parentheses are shown.

intermolecular contacts with nitro-group oxygen atoms: $H(2A)\cdots O(6)$ (at $-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z) = 2\cdot33$ (3) Å and $H(4A)\cdots O(4)$ (at x, $\frac{1}{2}-y$, $\frac{1}{2}+z) = 2\cdot27$ (3) Å; $N(4)\cdots O(4) = 2\cdot964$ (3) and $N(2)\cdots O(6) = 3\cdot018$ (3) Å. The first of these contacts, together with the carboxylic acid dimer interaction, forms hydrogen-bond-linked ribbons approximately parallel to [101], while the second forms a lateral link to another ribbon.

The packing coefficients (PC = total molecular volume/unit-cell volume) for over 40 polynitro-organic compounds have been calculated (Holden & Dickinson, 1979), giving values ranging from 0·70 to 0·81. The PC's calculated for (I)–(IV), 0·77, 0·79, 0·80 and 0·79, respectively, are near the top of the range of these values, suggesting that crystal-packing efficiency is an important contribution to the high crystal densities of these compounds.

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Structure of 3-Benzylidenephthalide, C15H10O2

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Abstract. $M_r = 222$, $P2_1/n$, $a = 15\cdot166$ (2), $b = 8\cdot002$ (2), $c = 19\cdot013$ (2) Å, $\beta = 103\cdot64$ (1)°, $V = 2242\cdot27$ Å^3, $Z = 8$, $D_m = 1\cdot32$ (8), $D_x = 1\cdot32$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot7093$ Å, $\mu = 0\cdot81$ cm^{-1}, $F(000) = 928$, $T = 298$ K, final $R = 0\cdot047$ for 1890 observed reflections. The title compound has the Z configuration with two molecules in the asymmetric unit related by a pseudo twofold axis. The molecule is almost planar with the phenyl ring *trans* to the benzene ring fused to phthalide. The benzene ring is slightly distorted by the five-membered ring fused to it.

Introduction. It is known (Knight & Pattenden, 1975) that alkylphthalides exist in two isomeric forms, E and Z, which give different melting points. The assignment of the form is purely based on proton NMR data. The title compound and 3-ethylidenephthalide were synthesized and their transformation to the other form could be observed by photochemical procedures (Lin, Wang, Koh & Ko, 1984). The chemical shifts on the

vinyl protons of the two forms are 6·33, 6·90 for the title compound and 5·6, 5·8 for 3-ethylidenephthalide. It is somewhat dangerous to assign the structure according to such small differences, so to confirm whether the synthetic product is the Z or E form, the single-crystal structure analysis was undertaken.

Experimental. Crystal 0·05 × 0·3 × 0·6 mm. CAD-4 diffractometer. Unit-cell parameters refined by least-squares methods on the basis of 25 reflections, 2θ range 22 to 24°. D_m by flotation (n-hexane/CCl$_4$). $2\theta_{max} = 50°$. Ranges of h,k,l: 0 to 18, 0 to 9, -22 to 22. Three standard reflections monitored every 2 h: variation $<\pm3\%$. 4268 unique reflections, 1890 observed with $I \geq 2\sigma(I)$. $R = 0\cdot047$, $wR = 0\cdot030$, $S = 1\cdot71$ based on F. Weighting scheme from counting statistics. Structure solved by direct methods using *MULTAN* with 315 highest E's, 100 smallest E's and 2409 $\sum_2$ relationships. H atoms found in difference Fourier map after isotropic refinement and then refined. Other atoms refined anisotropically. $(\Delta/\sigma)_{max} = 0\cdot26$. Peaks in final map $-0\cdot19$ to $0\cdot14$ e Å^{-3}. Atomic

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