

The principal structural difference between the double bond in open-chain olefins and the strained double bond in 1,2-disubstituted cyclopropenes is the angle formed between the substituent and the double bond. In olefins it is usually about 120° , but in cyclopropenes this angle increases to $151\text{--}155^\circ$ (Allen, 1982; Domnin, Kopf, Keyaniyan & de Meijere, 1985). It turns out that this increase in angle is enough to ensure the same coplanar orientation of phenyl and cyclopropene rings in both compound (I) and in 2-methyl-3-phenyl-2-cyclopropenecarboxylic acid (Korp, Bernal & Fuchs, 1983). In general, the crystal and molecular structures of these compounds are similar, although in compound (I) the bond distances of the three-membered ring are longer. For C(1)—C(2) and C(2)—C(3) bonds this difference reaches 0.015 \AA and for C(1)—C(3) 0.023 \AA . The average phenyl-ring distances and the lengths of the bonds leading from the cyclopropene ring to the carbons of the carboxyl, phenyl and *tert*-butyl groups are also longer. The bond distances C—O in the carboxyl groups of both compounds are essentially the same. It is important to note that, although the carboxyl group also possesses the bisected conformation relative to the cyclopropene ring [corresponding dihedral angle $87.4(1)^\circ$], the hydroxyl O atom is the O atom that is nearest to the three-membered ring, in contrast to the compound with the methyl substituent. Thus, one of the possible

explanations of the greater double-bond distance in compound (I) is the lack of interaction between the carbonyl group and the three-membered ring.

In the crystal structure of 2-*tert*-butyl-3-phenyl-2-cyclopropenecarboxylic acid, two molecules are combined by strong O—H \cdots O hydrogen bonds forming dimers across the inversion center. The O \cdots O separation is $2.657(2)$, O \cdots H is $1.681(8)\text{ \AA}$ and the O—H \cdots O angle is $174.7(8)^\circ$.

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Structure of 2,4,*N*-Trinitroanilinoacetic Acid

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Abstract. $\text{C}_8\text{H}_6\text{N}_4\text{O}_8$, $M_r = 286.2$, monoclinic, $P2_1/n$, $a = 10.417(1)$, $b = 10.396(1)$, $c = 10.880(1)\text{ \AA}$, $\beta = 108.61(1)^\circ$, $V = 1116.6(2)\text{ \AA}^3$, $Z = 4$, $D_m = 1.68$, $D_x = 1.70\text{ Mg m}^{-3}$, $\lambda(\text{Cu K}\alpha) = 1.5418\text{ \AA}$, $\mu = 12.46\text{ cm}^{-1}$, $F(000) = 584$, $T = 293\text{ K}$, final $R = 0.040$ for 1374 unique reflections [$I \geq 3\sigma(I)$]. In the molecule the phenyl ring is slightly non-planar. The

oxygens of the carboxylic group dimerize across a centre of inversion forming hydrogen bonds with O—H \cdots O distance $2.686(3)\text{ \AA}$ and angle $172(3)^\circ$.

Introduction. Aromatic amines and nitro compounds have a pivotal role in the synthetic chemistry of benzene. The nitro-group substitution results in a dramatic increase in the density of the compound. Several high-density nitro organics have been studied

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to relate molecular structure, crystal packing and density (Ammon & Prasad, 1985; Ammon & Bhattacharjee, 1982; Ammon, Bhattacharjee & Holden, 1982; Bhattacharjee & Ammon, 1981). The title compound, an aromatic nitramine, is one such example of a high-density nitro organic.

Experimental. D_m approximately measured by floatation, crystal of dimensions $0.50 \times 0.25 \times 0.20$ mm, Enraf-Nonius CAD-4 four-circle single-crystal diffractometer, cell parameters and standard deviations by least-squares analysis of measured θ angles (45 to 60°) of 25 normal reflections, systematic absences indicated $P2_1/n$, nickel-monochromated $\text{Cu K}\alpha$, $\omega-2\theta$ scan, scan width $\Delta\omega = (1.00 + 0.14\tan\theta)^\circ$, two standard reflections 283 and 391 with no significant intensity variation, 3622 reflections measured, $\theta = 2$ to 60° , $h - 11$ to 11 , $k 0$ to 11 and $l - 12$ to 12 , 1381 unique reflections with $I \geq 3\sigma(I)$, no absorption correction, direct methods with *SHELX76* (Sheldrick, 1976), all non-hydrogen atoms located from *E* map, refined by full-matrix least squares, anisotropic thermal parameters for all the non-hydrogen atoms, all hydrogens located from difference electron density maps and refined isotropically, $\sum w(|F_o| - |F_c|)^2$ minimized, $w^{-1} = [\sigma^2(F_o) + g|F_o|^2]$ with $g = 1.064 \times 10^{-3}$, $R = 0.040$ and $wR = 0.043$, after omitting the reflections $\bar{3}01$, 202 , $\bar{1}22$, $\bar{3}03$, $\bar{3}77$, 525 and $\bar{1},11,4$ from refinement, max. $\Delta/\sigma = 0.30$, excluding hydrogen atoms, max. and min. peak heights in the final electron density map of 0.21 and -0.37 e \AA^{-3} respectively; the atomic scattering factors were from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965), and the anomalous-dispersion corrections from Cromer & Liberman (1970).

Discussion. Table 1 lists the fractional coordinates of the non-hydrogen atoms with their equivalent isotropic temperature factors.* An *ORTEP* plot (Johnson, 1965) of the molecule excluding the hydrogen atoms is shown in Fig. 1. The bond lengths and bond angles between non-hydrogen atoms in the molecule are depicted in Fig. 2.

The C—C bonds in the aromatic ring on either side of the nitro substitution are shorter than those in the unsubstituted benzene. The C(1)—C(2) bond is an exception, the length being almost equal to the normal value. This is probably due to the *N*-substitution at the C(1) site. These trends in bonding pattern have been noticed in many amino nitro

Table 1. Fractional positional parameters ($\times 10^4$) of non-hydrogen atoms with equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}
C(1)	-178 (2)	385 (2)	7190 (2)	29 (1)
C(2)	-1525 (2)	798 (2)	6877 (2)	32 (1)
C(3)	-2550 (2)	219 (2)	5911 (2)	34 (1)
C(4)	-2216 (2)	-822 (2)	5288 (2)	34 (1)
C(5)	-920 (2)	-1305 (2)	5612 (2)	37 (1)
C(6)	108 (2)	-680 (2)	6559 (2)	33 (1)
N(1)	925 (2)	1012 (2)	8118 (1)	33 (1)
N(2)	-1896 (2)	1866 (2)	7584 (2)	38 (1)
O(1)	-2855 (2)	2542 (2)	7000 (2)	53 (1)
O(2)	-1231 (2)	2005 (2)	8728 (1)	51 (1)
N(3)	-3303 (2)	-1434 (2)	4234 (2)	43 (1)
O(3)	-3016 (2)	-2409 (2)	3751 (2)	58 (1)
O(4)	-4409 (2)	-931 (2)	3895 (2)	64 (1)
N(4)	1109 (2)	2302 (2)	7963 (2)	39 (1)
O(5)	402 (2)	2800 (1)	6963 (2)	48 (1)
O(6)	1979 (2)	2832 (2)	8845 (2)	53 (1)
C(7)	1609 (2)	459 (2)	9384 (2)	38 (1)
C(8)	3100 (2)	267 (2)	9636 (2)	37 (1)
O(7)	3695 (2)	-150 (2)	10183 (2)	50 (1)
O(8)	3652 (2)	478 (2)	8826 (2)	55 (1)

organics (Cady, 1967; Holden, Dickinson & Bock, 1972; Ammon & Prasad, 1985). The increase in the interior angles in the ring at the nitro substitution from 120° has been attributed to electron withdrawal by the nitro group changing the hybridization of the carbon atom (Carter, McPhail & Sim, 1966). The deviations of the other interior angles in the ring from 120° are in agreement with those reported (Domenicano & Murray-Rust, 1979).

There is an inverse correlation between the C—N bond length and the average length of the adjacent C—C bonds in the ring at amino and nitro substitutions. This can be explained as a result of electron withdrawal by the nitro groups *ortho* and *para* to an amino substitution in the aromatic ring (Holden & Dickinson, 1977).

The replacement of the hydrogens in the amino group by the nitro and carboxyl groups has resulted in an increase in C—N bond length from 1.327 (2) to 1.423 (2) \AA (Cady, 1967). The increase of O—N—O angles from 120 to 126.6 (2), 124.4 (2) and 124.5 (2) $^\circ$ can be reasoned as due to repulsion between the oxygens and the change of hybridization of the orbitals of the nitrogen atom (Holden & Dickinson, 1977).

The endocyclic torsion angles in the ring about C(6)—C(1), C(1)—C(2) and the other adjacent bonds are 1.5 (3), -3.8 (3), 2.5 (3), 1.2 (3), -3.4 (3) and 1.9 (3) $^\circ$ suggesting a minor deformation towards a twist-boat model. The *o*-nitro group is twisted from the ring plane by 31.6° while the *p*-nitro group is twisted through 6.7° only. This is to be expected due to steric hindrance between the bulky substituent at C(1) and the nitro group at C(2). To some extent the steric hindrance is also relieved by the increase in exocyclic angles at C(1) and C(2).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles, torsion angles and mean-plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52789 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bond features are normal in the acetic acid moiety. The oxygens O(7) and O(8) dimerize across a centre of inversion forming hydrogen bonds (Fig. 3), the O(7)—H(6)···O(8) distance and angle being 2.686 (3) Å and 172 (3)° respectively. The distance

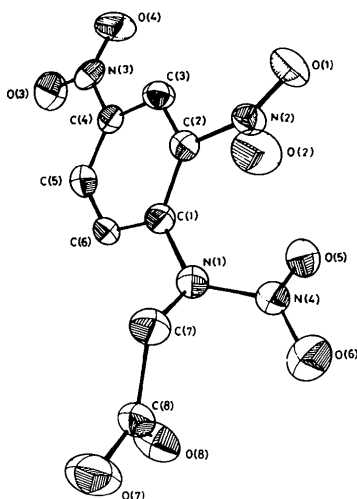


Fig. 1. Perspective view of the molecule.

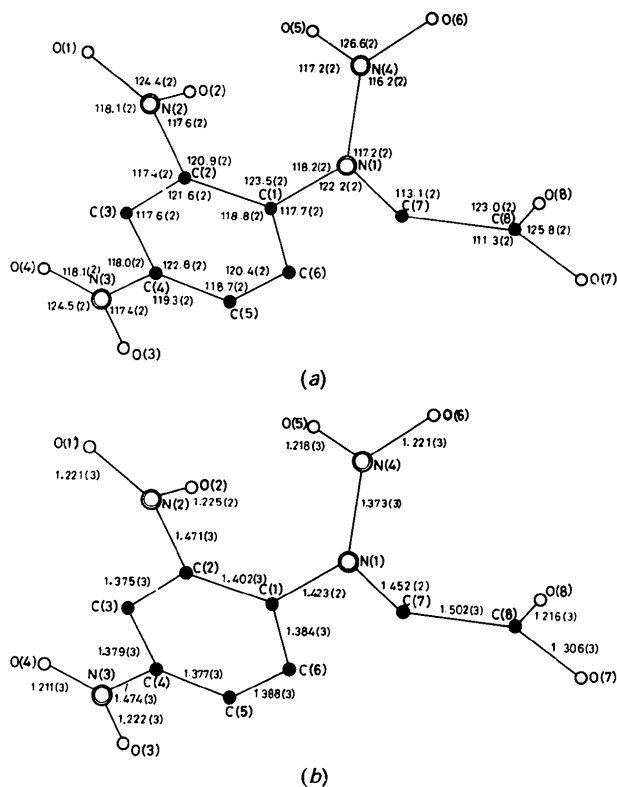


Fig. 2. (a) Bond angles (°) and (b) bond lengths (Å) between non-hydrogen atoms.

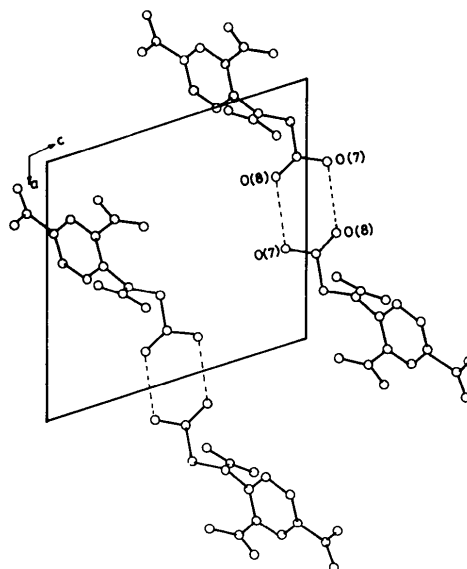


Fig. 3. Projection of the molecule down *b*.

between O(8) and H(6) is 1.83 (4) Å. The dimer is perfectly planar but the hydrogen H(6) is 0.08 Å away from the plane of the dimer. A projection of the molecular packing is shown in Fig. 3.

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