This molecule is remarkable for the high degree of unsaturation of ring *D*: C(14)—C(15) and C(17)—C(18) are typical double bonds with lengths 1·327 (8) and 1·339 (8) Å respectively. Amongst the known scalarane derivatives, only a few possess an ethyl group at C(4). In the present case, this ethyl group was determined in an axial position, in agreement with the X-ray analysis of (20*S*, 24*S*)-20-acetoxy-12β-hydroxy-20,24-dimethyl-25-norscalar-17-ene-18,24-carbolactone isolated from a *Carteriospongia* sp. (Croft, Ghisalberti, Skelton & White, 1983). Kikuchi, Tsukitani, Shimizu, Kobayashi & Kitagawa (1981) isolated foliaspongin from an Okinawan sample of *Carteriospongia foliascens*. On the basis of ^{13}C NMR arguments, they proposed the C(4) ethyl group to be equatorial. Comparison of these ^{13}C NMR data with those of our molecule leads us to correct this attribution and to propose an axial position for the ethyl group in foliaspongin. Bond distances and angles are given in Table 2.

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Crystallographic Studies and Physicochemical Properties of π-Electron Compounds. IV. Structure of 2,5-Dinitrobenzoic Acid (2,5-DNBA), $C_7H_4N_2O_6$

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Abstract. $M_r = 212{\cdot}12$, monoclinic, $C2/c$, $a = 12{\cdot}5512$ (9), $b = 11{\cdot}8834$ (9), $c = 11{\cdot}5880$ (9) Å, $\beta = 108{\cdot}882$ (6)°, $V = 1635{\cdot}35$ Å^3, $Z = 8$, $D_m = 1{\cdot}68$, $D_x = 1{\cdot}681$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 13{\cdot}82$ cm^{-1}, $F(000) = 864$, room temperature. The final R is 0·0359 for 962 counter intensities. The mean e.s.d.'s of bond lengths between the heavy atoms are 0·003 Å. The molecules are paired by hydrogen bonding between the carboxy groups [O—H···O 2·621 (2) Å], the two halves of the dimer being related by a centre of symmetry. The planes of the two carboxy groups in the dimer are separated by 0·023 Å. Non-additivity of substituent effects on the geometry of the benzene ring is observed for angles at C(1), C(5) and C(6) when the Domenicano & Murray-Rust [*Tetrahedron Lett.* (1979), **24**, 2283–2286] angular parameters are applied to DNBA.

Introduction. The crystal and, in particular, molecular structures of dinitrobenzoic acids are of interest because of the strong and naturally similar electronic properties of the substituents. Hence their influence on ring geometry has in recent years often been studied (Colapietro, Domenicano & Marciante, 1982; Więckowski & Krygowski, 1985).

Experimental. Pale-yellow prismatic crystals grown from an aqueous solution of the commercial product (Fluka). Monoclinic symmetry from oscillation and Weissenberg photographs. Crystal, *ca* 0·3 × 0·3 × 0·25 mm, mounted on a Syntex $P2_1$ single-crystal diffractometer. D_m measured at 293 K by flotation in chloroform–bromoform. Systematic absences: hkl $h+k$ odd, $h0l$ l odd, space group $C2/c$ or Cc. Cell constants determined by least-squares treatment of 15 reflexions with 2θ values between 11·7 and 31·2°. Intensities collected at room temperature using Cu $K\alpha$ radiation monochromated by graphite up to $2\theta = 115{\cdot}0°$, $h = -13$ to 12, $k = 0$ to 12, $l = 0$ to 12. Profile analysis according to Lehmann & Larsen (1974), no significant variation for 2 standard reflexions.

1140 unique intensities collected, of which 962 classified as observed, 54 of them systematically absent, other reflexions being suppressed on the criterion

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$I_o < 1\cdot962\sigma(I)$ [$\sigma(I)$ from counting statistics]. Corrections for Lorentz–polarization effects, but not for extinction or absorption. Structure solved by routine application of *SHELX*76 (Sheldrick, 1976). E map gave all C, N, O atomic positions, H atoms located from ΔF map. Structure factor calculation based on the positional parameters for the non-H atoms taken from E maps gave an R of 0·43, which reduced to 0·13 by isotropic least-squares refinement, and then to 0·083 by anisotropic refinement. Final refinement of all the atomic parameters, including the positional and isotropic thermal parameters of the H atoms, was carried out by full-matrix least squares and led to $R = 0\cdot0359$ with unit weights. The use of weights based on $\sigma(F)$ did not improve the R value or e.s.d.'s for positional parameters. Number of observations per refined parameter: $936/152 = 6\cdot2$. $(\Delta/\sigma)_{\max}$ in final cycle of refinement = 0·022, average = 0·009. Peaks in final difference Fourier map −0·18 to 0·12 e Å^{-3}.

Table 1. *Final coordinates* ($\times 10^4$) *for non-hydrogen atoms and equivalent isotropic thermal parameters* ($\times 10^3$)

$U_{\rm eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	$U_{\rm eq}$(Å^2)
C(1)	2723 (2)	3980 (2)	5616 (2)	30 (1)
C(2)	1621 (2)	4075 (2)	4829 (2)	32 (1)
C(3)	722 (2)	3576 (2)	5061 (2)	36 (2)
C(4)	913 (2)	2952 (2)	6117 (2)	40 (2)
C(5)	1991 (2)	2879 (2)	6916 (2)	35 (1)
C(6)	2894 (2)	3372 (2)	6689 (2)	33 (1)
C(7)	3713 (2)	4451 (2)	5344 (2)	33 (1)
N(1)	1356 (2)	4740 (2)	3700 (2)	36 (1)
N(2)	2198 (2)	2237 (2)	8059 (2)	47 (1)
O(1)	3564 (1)	4970 (2)	4371 (2)	49 (2)
O(2)	4667 (2)	4263 (2)	6111 (2)	51 (1)
O(3)	1285 (2)	4250 (2)	2759 (2)	55 (1)
O(4)	1178 (2)	5736 (2)	3777 (2)	53 (1)
O(5)	3105 (2)	2357 (2)	8853 (2)	55 (1)
O(6)	1441 (2)	1626 (2)	8138 (2)	68 (1)

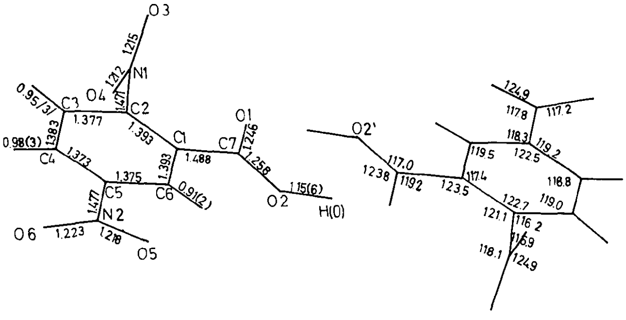


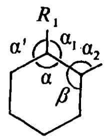
Fig. 1. Projection of the dimer of 2,5-DNBA along **c**. Assignments of atoms are consistent with those used in Table 1. Bond lengths in Å, bond angles in degrees. Estimated standard deviations are 0·003 Å for bonds not involving H atoms, 0·2° for angles not involving H atoms. The O(1)···O(2′) hydrogen-bond length is 2·621 Å. The symmetry operation relating O(2) to O(2′) is $1-x$, $1-y$, $1-z$.

The equations of the least-squares planes, the torsion angles and other geometrical data were calculated using *PLANE* (Jaskólski, 1981*a*) and *GEOME* (Jaskólski, 1981*b*).

Discussion. The final atomic parameters are given in Table 1. Bond lengths and angles are given in Fig. 1. They have not been corrected for the effects of thermal motion.

The mean-plane calculations and angles between the best planes have been deposited.*

The deviations of ring geometry from D_{6h} ($6/mmm$) symmetry are highly significant and involve bond distances as well as angles. The valence angle at the carbon substituted by COOH should be about 120° for unsubstituted and *para*-substituted benzoic acids (Domenicano, Vaciago & Coulson, 1975). It was found for benzoic acid (Feld, Lehmann, Muir & Speakman, 1981) that $\alpha_{\rm COOH} = 119\cdot67$ and 120·1° after correction for molecular libration, for *p*-nitrobenzoic acid $\alpha_{\rm COOH} = 120\cdot4°$ (Colapietro & Domenicano, 1977) and for another modification 120·0° (Groth, 1980). In the 2,5-DNBA molecule $\alpha_{\rm COOH} = 117\cdot4°$. Similar values are observed for other *ortho*-substituted benzoic acids with the NO_2 group in the *ortho* position: 2,4-dinitrobenzoic acid (2,4-DNBA) 117·9° (Więckowski & Krygowski, 1985). If there are no interactions between *ortho* substituents $\sum\alpha = \alpha_1 + \alpha_2 = 360° - (\alpha/2 + \beta/2) = 240°$.



In many cases it is seen that $\sum\alpha > 240°$, *e.g.* for 2,5-DNBA it is 244·6°, for 2,4-DNBA 245·2°, whereas for *o*-nitrobenzoic acid it is 243·8°. This obviously leads to a diminution of α and α′ angles.

In contrast to the above finding for $\alpha_{\rm COOH}$, the α values at C atoms substituted by the NO_2 group do not differ from the literature data for other nitrobenzoic acids.

The substituents in 2,5-DNBA cause nonadditive changes in the geometry of the benzene ring. Applying the Domenicano & Murray-Rust (1979) angular substituent parameters to 2,5-DNBA and, for comparison, to 2,4-DNBA and *o*-nitrobenzoic acid one obtains the results shown in Table 2. It is immediately apparent that only angles at C(1), C(5) and C(6) are

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, mean-plane calculations and dihedral angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42166 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Experimental values of angles in the benzene ring and the difference between these and the values obtained from the Domenicano & Murray-Rust rules* (*Δ, in degrees*)

2,5-Dinitrobenzoic acid		2,4-Dinitrobenzoic acid		*o*-Nitrobenzoic acid	
Angle	*Δ*	Angle	*Δ*	Angle	*Δ*
117·4	−1·1	117·9	−0·7	116·2	−2·0
122·7	−0·4	122·9	−0·1	123·7	0·0
119·0	0·5	116·6	0·3	118·4	0·2
118·8	0·2	123·4	0·0	120·6	0·1
122·5	−0·9	118·2	−0·4	119·8	−0·7
119·5	1·3	120·9	0·5	121·2	1·1

distinctly deformed in comparison with the values expected by the additive influence of substituents.

The benzene ring and carboxyl group are nearly coplanar for 2,5-DNBA, the angle between the planes being 4·0°. The NO_2 substituent in the *ortho* position is nearly perpendicular to the benzene ring, with interplanar angle 86·0°. The angle between the planes of the carboxy and nitro groups in the *ortho* position is 89·8°. A similar finding is observed for 2,4-DNBA (Więckowski & Krygowski, 1985), the angle between neighbouring NO_2 and COOH substituents being 64·4°. For *o*-nitrobenzoic acid the carboxy and nitro groups make angles of 24·1° and 54·3°, respectively, with the aromatic plane (Tavale & Pant, 1973), and consequently the angle between COOH and NO_2 planes is 78·4°. On comparison of the above-mentioned structures we can say that neighbouring NO_2 and COOH groups are twisted by an angle of 60–90°.

The planes of the benzene ring and of the other nitro group are nearly coplanar. The angles found are: for *p*-nitrobenzoic acid 13·7° (Colapietro & Domenicano, 1977), 2,5-DNBA 14·3°, 2,4-DNBA 4·1° (Więckowski & Krygowski, 1985), *m*-nitrobenzoic acid 2·7 and 1·3° for *A* and *B* forms (Dhaneshwar, Kulkarni, Tavale & Pant, 1975). These results are in line with the conclusions of Holden & Dickinson (1977).

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Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic Anhydride (1), $C_9H_6O_3$, and Bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylic Anhydride (2), $C_9H_8O_3$

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Abstract. (1) $M_r = 162{\cdot}15$, monoclinic, $P2_1/n$, $a = 12{\cdot}642\ (3)$, $b = 11{\cdot}412\ (2)$, $c = 11{\cdot}773\ (2)$ Å, $\beta = 117{\cdot}77\ (2)°$, $V = 1502{\cdot}9\ (6)$ Å^3, $Z = 8$, $D_x = 1{\cdot}433$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 9{\cdot}30$ cm^{-1}, $F(000) = 672$, $T = 298$ K, $R = 0{\cdot}046$ for 1498 independent observed reflections. (2) $M_r = 164{\cdot}16$, orthorhombic, $Pnma$, $a = 6{\cdot}233\ (2)$, $b = 10{\cdot}421\ (4)$, $c = 11{\cdot}843\ (4)$ Å, $V = 769{\cdot}3\ (5)$ Å^3, $Z = 4$, $D_x =$

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