

chair C1–C6. As a result the *tert*-butyl groups occupy positions intermediate between equatorial and axial.

The shortest intermolecular H–H distance is 2.36 Å, in agreement with the hydrogen van der Waals diameter of 2.34 Å. The double-bond length of 1.339 (3) Å is equal to that reported by Sasvári & Löw.

The molecules are held together by van der Waals interactions.

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Structure of Hexacyclo[7.4.2.0^{1,9}.0^{3,7}.0^{4,14}.0^{6,15}]pentadeca-10,12-diene-2,8-dione*

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Abstract. C₁₅H₁₂O₂, *M_r* = 224.25, monoclinic, *P*2₁/*n*, *a* = 7.192 (1), *b* = 10.821 (1), *c* = 14.093 (2) Å, β = 97.48 (1)°, *V* = 1087.5 (2) Å³, *Z* = 4, *D_m* = 1.34 (1), *D_x* = 1.36 (1) Mg m⁻³, λ(Cu *K*α) = 1.5418 Å, μ = 0.729 mm⁻¹, *F*(000) = 472, *T* = 293 K, *R* = 0.055 (*wR* = 0.056) for 1323 observed reflections. The carbon skeleton consists of four 'envelope' five-membered rings, one planar four-membered ring and two six-membered rings. The diene ring is planar while the dione-bearing ring has a boat conformation.

Introduction. The transformation of aromatics to cycloalkanes *via* strained polycyclic systems is increasingly becoming a standard synthetic protocol towards complex organic natural products (Wender, 1983; Solott & Gilbert, 1980; Eaton, Ravi Shanker, Price, Pluth, Gilbert, Alster & Sandus, 1984). The nature of bonding in the cyclobutane-ring framework of polycyclic systems of cubane and homocubane is also of interest. With a view to examine whether [2+2]-*ortho* addition or [3+2]-*meta* addition (Mehta,

- References**
- ASVELD, W. H. & KELLOGG, R. M. (1982). *J. Org. Chem.* **47**, 1250–1257.
- DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*. New York: IFI/Plenum Data Company.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- KELLOGG, R. M. & KAISER, J. K. (1975). *J. Org. Chem.* **40**, No. 17, 2575.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- SASVÁRI, K. & LÖW, M. (1965). *Acta Cryst.* **19**, 840.
- SHELDRICK, J. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Murthy, Reddy & Reddy, 1986; Bryce-Smith & Gilbert, 1976) is operative in an intramolecular benzene olefin photoaddition, the major Diels–Alder isomer of cyclopentadiene and 1,4-naphthoquinone was irradiated at 254 nm and crystals were obtained by repeated slow crystallization from a 3:1 mixture of petroleum ether and benzene. The X-ray structure was essential for stereoselective synthetic manipulations of the diene functionality.

Experimental. Crystal ~0.1 × 0.25 × 0.8 mm, *D_m* by flotation in aqueous KI, Nonius CAD-4F-11M diffractometer, Cu *K*α radiation, ω/2θ scan mode, scan speed 1° min⁻¹, θ ≤ 60°, 0 ≤ *h* ≤ 8, 0 ≤ *k* ≤ 12, -15 ≤ *l* ≤ 15, 1708 reflections collected, 1323 judged significant [*|F_o*| > 3σ(*|F_o*|)], lattice parameters from 25 reflections (16.5 ≤ 2θ ≤ 51.8°), three standard reflections (501, 228 and 244) every 2000 s, 4% variation in intensity. No correction for absorption. Structure solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement (on *F*) of scale factor, positional and anisotropic thermal parameters for H atoms, initial H positions

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for non-hydrogen atoms with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}accos\beta).$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
C(1)	870 (4)	-1169 (3)	6337 (2)	2.81
C(2)	2758 (5)	-677 (3)	6155 (2)	3.12
C(3)	3870 (5)	-1776 (3)	5915 (2)	3.49
C(4)	2482 (5)	-2520 (4)	5216 (2)	3.86
C(5)	2952 (6)	-3865 (3)	5431 (3)	4.49
C(6)	2879 (5)	-3763 (3)	6504 (3)	3.76
C(7)	4163 (5)	-2672 (3)	6828 (2)	3.52
C(8)	3237 (5)	-2088 (3)	7627 (2)	3.16
C(9)	1160 (4)	-2061 (3)	7247 (2)	2.88
C(10)	-168 (5)	-1870 (3)	7967 (2)	3.63
C(11)	-1576 (5)	-1075 (4)	7821 (3)	3.87
C(12)	-1837 (5)	-276 (4)	6991 (3)	4.12
C(13)	-695 (5)	-281 (3)	6324 (3)	3.74
C(14)	608 (5)	-2337 (3)	5676 (2)	3.28
C(15)	926 (5)	-3206 (3)	6564 (2)	3.35
O(1)	3240 (4)	407 (2)	6180 (2)	4.72
O(2)	3970 (3)	-1716 (3)	8395 (2)	4.35

Table 2. Bond distances (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses

C(1)–C(2)	1.511 (5)	C(6)–C(7)	1.531 (5)
C(1)–C(9)	1.598 (4)	C(6)–C(15)	1.540 (5)
C(1)–C(13)	1.478 (5)	C(7)–C(8)	1.518 (4)
C(1)–C(14)	1.568 (4)	C(8)–C(9)	1.520 (5)
C(2)–C(3)	1.496 (5)	C(8)–O(2)	1.210 (4)
C(2)–O(1)	1.222 (4)	C(9)–C(10)	1.696 (4)
C(3)–C(4)	1.535 (5)	C(9)–C(15)	1.565 (4)
C(3)–C(7)	1.602 (4)	C(10)–C(11)	1.324 (5)
C(4)–C(5)	1.515 (5)	C(11)–C(12)	1.447 (6)
C(4)–C(14)	1.581 (5)	C(12)–C(13)	1.326 (6)
C(5)–C(6)	1.524 (6)	C(14)–C(15)	1.559 (4)
C(2)–C(1)–C(9)	108.8 (2)	C(6)–C(7)–C(8)	103.7 (3)
C(2)–C(1)–C(13)	118.0 (3)	C(7)–C(8)–C(9)	104.6 (3)
C(2)–C(1)–C(14)	102.9 (2)	C(7)–C(8)–O(2)	128.3 (3)
C(9)–C(1)–C(13)	115.0 (3)	C(9)–C(8)–O(2)	127.0 (3)
C(9)–C(1)–C(14)	89.0 (2)	C(1)–C(9)–C(8)	108.3 (2)
C(13)–C(1)–C(14)	119.0 (3)	C(1)–C(9)–C(10)	115.6 (2)
C(1)–C(2)–C(3)	106.1 (3)	C(1)–C(9)–C(15)	89.5 (2)
C(1)–C(2)–O(1)	126.2 (3)	C(8)–C(9)–C(10)	116.7 (3)
C(3)–C(2)–O(1)	127.7 (3)	C(8)–C(9)–C(15)	102.9 (2)
C(2)–C(3)–C(4)	103.9 (3)	C(10)–C(9)–C(15)	120.0 (3)
C(2)–C(3)–C(7)	108.5 (3)	C(9)–C(10)–C(11)	121.8 (3)
C(4)–C(3)–C(7)	101.8 (3)	C(10)–C(11)–C(12)	122.1 (4)
C(3)–C(4)–C(5)	105.4 (3)	C(11)–C(12)–C(13)	122.9 (4)
C(3)–C(4)–C(14)	100.9 (3)	C(1)–C(13)–C(12)	122.3 (3)
C(5)–C(4)–C(14)	102.6 (3)	C(1)–C(14)–C(4)	107.6 (3)
C(4)–C(5)–C(6)	95.3 (3)	C(1)–C(14)–C(15)	90.9 (2)
C(5)–C(6)–C(7)	104.8 (3)	C(4)–C(14)–C(15)	102.1 (3)
C(5)–C(6)–C(15)	103.4 (3)	C(6)–C(15)–C(9)	108.5 (3)
C(7)–C(6)–C(15)	101.6 (3)	C(6)–C(15)–C(14)	103.4 (3)
C(3)–C(7)–C(6)	102.5 (3)	C(9)–C(15)–C(14)	90.5 (2)
C(3)–C(7)–C(8)	108.6 (3)		

(calculated by stereochemistry and confirmed by difference Fourier map) converged to $R = 0.055$, $wR = 0.056$, $S = 1.79$, $w(|F_o| - |F_c|)^2$ minimized, $w = (2.0 + 1.0|F_o| + 0.033|F_o|^2)^{-1}$, $(\Delta/\sigma)_{\max} = 0.10$. Final $\Delta\rho$ excursions $< |0.3| e \text{\AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Program *LALS* (Gantzel, Sparks & Trueblood, 1961) used for refinement.

Discussion. The atomic coordinates with their e.s.d.'s and equivalent isotropic temperature factors are given in Table 1.* Bond lengths and bond angles involving the non-H atoms are given in Table 2. Fig. 1 shows a perspective view of the molecule.

The carbon skeleton is made up of four five-membered rings, one four-membered ring and two six-membered rings. The molecule is 'cage-like' with one edge (the dione side) open. All the five-membered rings are in 'envelope' conformation. The four-membered ring is planar with an average dihedral angle between the two halves along the diagonals of $1.3 (5)^\circ$. This may be compared with the angle of $19.5 (6)^\circ$ found in 6,6,10,10-tetranitropentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]-decane (George, Gillardi, Flippen-Anderson, Choi, Marchand & Reddy, 1985) and about 20° in the case of polynitro-bishomocubane (Ammon, Zhang, Choi, Sandus, Marchand & Suri, 1985) indicating the amount of strain on 'cage' formation. The six-membered diene ring is planar with $C(10)–C(11) = 1.324 (5)$ and $C(12)–C(13) = 1.326 (6)$ \AA depicting the double-bond character. The other six-membered ring consisting of atoms C(1), C(2), C(3), C(7), C(8) and C(9) has a boat conformation.

Chemically similar bonds (Watson, Marchand & Dave, 1987) viewed down the end at C(2) and C(8) are internally consistent, *i.e.* $C(2)–C(3) = 1.496 (5)$, $C(8)–C(7) = 1.518 (4)$; $C(3)–C(4) = 1.535 (5)$, $C(6)–C(7) = 1.531 (5)$; $C(1)–C(2) = 1.511 (5)$, $C(8)–C(9) = 1.520 (5)$ \AA *etc.* except in the case of $C(4)–C(14) = 1.581 (5)$, $C(6)–C(15) = 1.540 (5)$ \AA . This may be attributed to the fact that the coordinates of C(4) are nearly at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$. The norbornane ring has a

* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51287 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

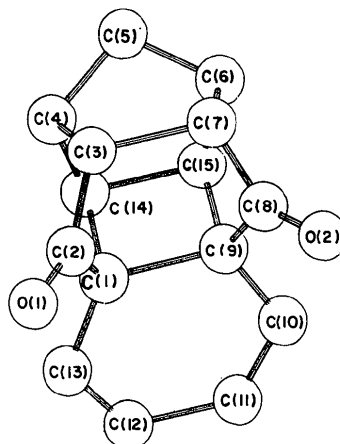


Fig. 1. A perspective view of the title molecule.

synchro twist $S(++)$ (Acharya, Tavale & Guru Row, 1984).

The molecules are held together by van der Waals interactions.

References

- ACHARYA, K. R., TAVALE, S. S. & GURU ROW, T. N. (1984). *Proc. Indian Acad. Sci. (Chem. Sci.)*, **93**, 271–282.
- AMMON, H. L., ZHANG, D., CHOI, C. S., SANDUS, O., MARCHAND, A. P. & SURI, S. C. (1985). *Acta Cryst.* **C41**, 404–406.
- BRYCE-SMITH, D. & GILBERT, A. (1976). *Tetrahedron*, **32**, 1309–1326.
- EATON, P. E., RAVI SHANKER, B. K., PRICE, G. D., PLUTH, J. J., GILBERT, E. E., ALSTER, J. & SANDUS, O. (1984). *J. Org. Chem.* **49**, 185–186.
- GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). *LALS*. Program for the full-matrix refinement of positional and thermal parameters and scale factors. Univ. of California, USA.
- GEORGE, C., GILLARDI, R., FLIPPEN-ANDERSON, J. L., CHOI, C. S., MARCHAND, A. P. & REDDY, D. S. (1985). *Acta Cryst.* **C41**, 788–791.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MEHTA, G., MURTHY, A. N., REDDY, D. S. & REDDY, A. V. (1986). *J. Am. Chem. Soc.* **108**, 3443–3452.
- SOLOTT, G. P. & GILBERT, G. E. (1980). *J. Org. Chem.* **45**, 5405–5408.
- WATSON, W. H., MARCHAND, A. P. & DAVE, P. R. (1987). *Acta Cryst.* **C43**, 1569–1571.
- WENDER, P. A. (1983). *Selectivity – A Goal for Synthetic Efficiency*, edited by W. BARTMAN & B. M. TROST, pp. 335–348. Berlin: Verlag Chemie.

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Structure of 2-Amino-4-(methylphosphinico)butyric Acid Hydrochloride

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Abstract. $C_5H_{13}NO_4P^+Cl^-$, $M_r = 217.8$, monoclinic, $P2_1/n$, $a = 12.642$ (5), $b = 5.474$ (3), $c = 14.233$ (5) Å, $\beta = 105.10$ (5)°, $V = 950.9$ Å³, $Z = 4$, $D_m = 1.52$ (1), $D_x = 1.52$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 0.55$ mm⁻¹, $F(000) = 456$, $T = 292$ K, $R = 0.038$ for 1359 observed reflexions. The molecule exists in a cationic form in which the amino group is protonated and the carboxylic and the phosphinic acid groups are neutral. The N–C–COOH moiety is nearly planar, the torsion angle ψ' is -2.0 (4)°; C ν (1) is *gauche* to both C(4) and N with torsion angles χ^1 and χ^2 at -49.1 (4) and 73.8 (3)° respectively; P is *trans* to C α (3) [P–C ν (1)–C β (2)–C α (3) = -163.9 (3)°]. There is extensive intermolecular hydrogen bonding in the structure.

Introduction. It has been known for more than twenty years (Mastalerz, 1959) that the phosphonic and phosphinic acid analogues of glutamic acid possess inhibitory properties towards glutamine synthetase. Phosphinothricin [2-amino-4-(methylphosphinico)-butyric acid] has been isolated from cultures of *Streptomyces viridochromogenes* (Bayer *et al.*, 1972) and *Streptomyces hygroscopicus* as the tripeptide, phosphinothricinyl-alanyl-alanine. This tripeptide is active against Gram-positive and Gram-negative bacteria

and also against the fungi *Botrytis cinerea*, sheath blight and rice blast (Kondo *et al.*, 1973). The two alanine residues allow the penetration of this tripeptide through the cell wall. Inside the cell it is assumed that phosphinothricin is liberated by 'lethal cleavage of an inactive material'.

D,L-Phosphinothricin is an active glutamine synthetase inhibitor (Mastalerz, 1959; Leason, Cunliffe, Parkin, Lea & Mifflin, 1982) and shows herbicidal properties (Rupp, Finke, Beringer & Lagenlueddeke, 1977). Recently, the crystal structures of DL- and L-phosphinothricin have been reported by Paulus & Grabley (1982). This paper reports the first X-ray structure of an aminophosphinic acid hydrochloride.

Experimental. The free phosphinothricin was prepared by the method developed by Dr E. Gruszecka-Kowalik at the Institute of Organic and Physical Chemistry, Technical University of Wrocław, Poland. Clear colourless crystals were obtained by slow evaporation from a saturated aqueous solution with excess 20% hydrochloric acid. Crystal of dimensions $0.28 \times 0.40 \times 0.45$ mm: D_m by flotation in carbon tetrachloride/ethylene bromide: monoclinic $P2_1/n$ from Weissenberg photographs. Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation