The structure was solved using direct methods and refined by the full-matrix least-squares technique. All non-H atoms were refined with anisotropic displacement parameters. Weights calculated from counting statistics were employed as it was found that they provided a reliable estimate of the experimental error. The resulting averaged values of $w(\Delta F)^2$ as a function of $\sin\theta$ and F^2 did not show any significant variations.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *DREADD* (Blessing, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Johnson & Burnett, 1996).

We thank Mr Flemming Hansen for help with the crystallographic experiment.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1068). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.
Anthony, J., Knobler, C. B. & Diederich, F. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 406–409.
Bader, R. F. W. (1990). *Atoms in Molecules: A Quantum Theory*. Oxford: Oxford University Press.
Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
Bott, S. G., Marchand, A. P., Talafuse, L. K. & Rajagopal, D. (1995). *J. Chem. Cryst.* **25**, 543–547.
Bürgi, H. B. & Dunitz, J. D. (1994). *Structure Correlation*. Weinheim: VCH.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Hanson, A. W. (1975). *Acta Cryst.* B**31**, 831–834.
Johnson, C. K. & Burnett, M. N. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Kaftory, M., Agmon, I., Ladika, M. & Stang, P. J. (1987). *J. Am. Chem. Soc.* **109**, 782–787.
Kaftory, M., Yagi, M., Tanaka, K. & Toda, F. (1988). *J. Org. Chem.* **53**, 4391–4393.
Kane, J. J., Liao, R.-F., Lauher, J. W. & Fowler, F. W. (1995). *J. Am. Chem. Soc.* **117**, 12003–12004.
Lu, T., Menelaou, M. A., Vargas, D., Fronczek, F. R. & Fischer, N. H. (1993). *Phytochem.* **32**, 1483–1488.
Pilkington, M., Wallis, J. D. & Larsen, S. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1499–1500.
Pilkington, M., Wallis, J. D., Smith, G. T. & Howard, J. A. K. (1996). *J. Chem. Soc. Perkin Trans.* 2, pp. 1849–1854.
Rice, C. R. & Wallis, J. D. (1993). *J. Chem. Soc. Chem. Commun.* pp. 572–574.
Schweizer, W. B., Procter, G., Kaftory, M. & Dunitz, J. D. (1978). *Helv. Chim. Acta*, **61**, 2783–2808.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Toda, F., Tanaka, K. & Mak, T. C. W. (1989). *Chem. Lett.* pp. 1329–1330.
Tsibouklis, J., Werninck, A. R., Shand, A. J. & Milburn, G. H. W. (1988). *Chemtronics*, **3**, 211–214.

Acta Cryst. (1999). C**55**, 108–110

1,3,5-Tris(cyanomethyl)-2,4,6-triethylbenzene

Christian Walsdorff, Ki-Min Park, Jinho Oh and Kimoon Kim

Department of Chemistry and National Creative Research Initiative Centre for Smart Supramolecules, Pohang University of Science and Technology, San 31, Hyojadong, Pohang 790-784, Republic of Korea. E-mail: kkim@vision.postech.ac.kr

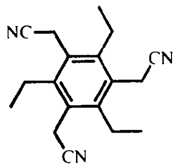
(*Received 6 August 1998; accepted 9 September 1998*)

Abstract

The title compound (2,4,6-triethyl-1,3,5-benzenetriacetonitrile, $C_{18}H_{21}N_3$) exhibits an unexpected conformation with all the substituents, except one cyanomethyl group, pointing to the same side of the plane of the benzene ring.

Comment

Hexa-substituted derivatives of benzene with the substituents connected *via* methylene groups to the central benzene ring have attracted considerable interest. In general, the most stable conformation of such compounds is the one with the substituents pointing alternately to both sides (above and below) of the plane of the central benzene ring. This conformational preference has been employed in an approach to 'hexa-host' clathrate compounds (MacNicol & Downing, 1996). More recently, derivatives with ethyl groups in the 1, 3 and 5 positions and substituents that carry functional groups attached to the remaining positions of the benzene ring have been used as predisposed (Stack *et al.*, 1993; Walsdorff *et al.*, 1996; Metzger *et al.*, 1997) or preorganized (Walsdorff *et al.*, 1997) tripodal ligands, in a self-directed macrocyclization (Bisson *et al.*, 1997) and in the spontaneous self-assembly of a cage compound (Hartshorn & Steel, 1997). In the course of our ongoing research on such molecules we have determined the crystal structure of the title compound, (I).



(I)

In spite of its symmetrical constitution, (I) crystallizes on a general position in the triclinic space group

$P\bar{1}$. The individual molecules of (I) are clearly separated. The metric parameters are normal and the central benzene ring does not deviate significantly from planarity. Surprisingly, the molecule adopts a conformation with all the substituents except one cyanomethyl group pointing to the same side of the central benzene ring.

Deviations from the alternating pattern among the substituents of molecules with a hexamethylenebenzene backbone have been occasionally observed in the crystal state. Such behaviour was ascribed to (i) the steric influence of bulky ligands attached to a metal that was η^6-coordinated to the central benzene ring (Iverson *et al.*, 1981), (ii) to some distortion from planarity of the hexamethylenebenzene framework caused by tension induced by tripodal coordination of a metal to the substituents (Hou *et al.*, 1997) or (iii) to intramolecular interactions by hydrogen bonds with solvate water molecules present in the crystal structure (Hoskins *et al.*, 1997). The conformation of (I) cannot be traced to any such influence.

According to molecular mechanics calculations (Autodesk, 1993) using the MM^+ force field, the conformation with the substituents pointing alternately to opposite directions of the central benzene plane is the most stable one in the gas phase, being some 18 kJ mol^{-1} lower in energy than the conformation observed in this crystal structure. In solution the NMR data at room temperature are consistent with the C_3 symmetry of the 'up-down' conformation, too. However, since the intramolecular factors that influence the conformation of the molecule are obviously overcome in the crystal state, we have to ascribe this to packing effects.

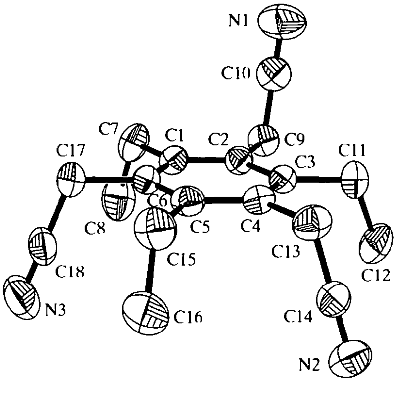


Fig. 1. The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity.

Experimental

(I) was prepared by a published procedure (Walsdorff *et al.*, 1996). Crystals suitable for X-ray crystallography were obtained by layering *n*-hexane onto a solution of (I) in dichloromethane at room temperature.

Crystal data

$C_{18}H_{21}N_3$
$M_r = 279.38$
Triclinic
$P\bar{1}$
$a = 8.2898\,(2)$ Å
$b = 9.7520\,(1)$ Å
$c = 11.2391\,(3)$ Å
$\alpha = 112.131\,(1)°$
$\beta = 96.654\,(1)°$
$\gamma = 104.437\,(1)°$
$V = 792.47\,(3)$ Å^3
$Z = 2$
$D_x = 1.171$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5009 reflections
$\theta = 2.90$–$28.32°$
$\mu = 0.070$ mm^{-1}
$T = 296\,(2)$ K
Block
0.55 × 0.50 × 0.45 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
φ and ω scans
Absorption correction: none
5009 measured reflections
3623 independent reflections
3122 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.041$
$\theta_{\rm max} = 28.32°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 14$
Intensity decay = 0.14%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.146$
$S = 1.072$
3623 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 0.1751P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.000$
$\Delta\rho_{\rm max} = 0.216$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.183$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data were collected over a hemisphere of reciprocal space, by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each exposure of 20 s covered 0.30° in ω. The crystal-to-detector distance was 5 cm. The first 50 frames were retaken after complete data collection. The crystal showed no significant decay and no correction was applied for absorption or decay. The structure was solved by direct methods. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms. H atoms were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which they are attached.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SHELXTL* (Sheldrick, 1996). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

The authors thank the Korean Science and Engineering Foundation (KOSEF) and the Korean Ministry of Science and Technology (Creative Research Initiatives) for support of this work. KMP is grateful to the Korea Research Foundation for his post-doctoral fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1001). Services for accessing these data are described at the back of the journal.

References

Autodesk (1993). *HyperChem Computational Chemistry Software.* Autodesk Inc., USA.

Bisson, A. P., Lynch, V. M., Monahan, M.-K. C. & Anslyn, E. V. (1997). *Angew. Chem.* **109**, 2435–2437; *Angew. Chem. Int. Ed. Engl.* **36**, 2340–2342.

Hartshorn, C. M. & Steel, P. J. (1997). *Chem. Commun.* pp. 541–542.

Hoskins, B. F., Robson, R. & Slizys, D. A. (1997). *Angew. Chem.* **109**, 2861–2863; *Angew. Chem. Int. Ed. Engl.* **36**, 2752–2755.

Hou, Z., Stack, T. D. P., Sunderland, C. J. & Raymond, K. N. (1997). *Inorg. Chim. Acta*, **263**, 341–355.

Iverson, D. J., Hunter, G., Blount, J. F., Damewood, J. R. & Mislow, K. (1981). *J. Am. Chem. Soc.* **103**, 6073–6083.

MacNicol, D. D. & Downing, G. A. (1996). *Comprehensive Supramolecular Chemistry*, Vol. 6, edited by D. D. MacNicol, F. Toda & R. Bishop, pp. 421–461. Oxford: Pergamon.

Metzger, A., Lynch, V. M. & Anslyn, E. V. (1997). *Angew. Chem.* **109**, 911–914; *Angew. Chem. Int. Ed. Engl.* **36**, 862–865.

Sheldrick, G. M. (1996). *SHELXTL*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT*. *Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stack, T. D. P., Hou, Z. & Raymond, K. N. (1993). *J. Am. Chem. Soc.* **115**, 6466–6467.

Walsdorff, C., Saak, W. & Pohl, S. (1996). *J. Chem. Res.* (*S*), pp. 282–283; *J. Chem. Res.* (*M*), pp. 1601–1618.

Walsdorff, C., Saak, W. & Pohl, S. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1857–1861.

Acta Cryst. (1999). C**55**, 110–112

2,2′-Biphenyl (cyclohexylamino)phosphonate: a hydrogen-bonded dimer

C. Muthiah and K. C. Kumara Swamy

School of Chemistry, University of Hyderabad, Hyderabad 500 046, AP, India. E-mail: kckssc@uohyd.ernet.in

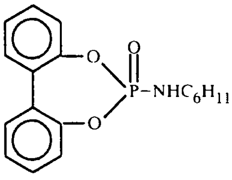
(*Received 2 April 1998; accepted 24 July 1998*)

Abstract

The structure of the title compound, $C_{18}H_{20}NO_3P$, reveals a hydrogen-bonding interaction between the NH group and the phosphoryl-O atom, resulting in a dimer; no interaction of the O atoms of the seven-membered 1,3,2-dioxaphosphepine ring with the NH proton is found.

Comment

We have recently described the structures of the amino phosphorus derivatives $(C_6H_{11}NH)P(OCH_2CMe_2CH_2O)$, (1), $(C_6H_{11}NH)P(OCH_2CMe_2CH_2O)(O_2C_6Cl_4)$, (2), $(C_6H_{11}NH)P[\{O\text{-}(^tBu)_2C_6H_2\}_2CH_2]$, (3), and $(C_6H_{11}NH)P[\{O\text{-}(^tBu)_2C_6H_2\}_2CH_2](O_2C_6H_4)$, (4) (Said *et al.*, 1997). Whereas the tricoordinated compounds, (1) and (3), showed hydrogen bonding involving $C_6H_{11}NH$ and an O atom of the six- or eight-membered ring, such a feature was absent in the pentacoordinated compounds, (2) and (4). In connection with this, we were interested in knowing the nature of the hydrogen bonding, if any, in cyclic phosphates bearing a primary amino group such as $C_6H_{11}NH$. Herein we report the results on one such phosphate, the title compound, $(C_6H_{11}NH)PO(2,2'\text{-}OC_6H_4\text{–}C_6H_4O)$, (5). Compound (5), with a tetracoordinated P atom, was also chosen in order to study any conformational changes in the seven-membered ring, compared with tri- or pentacoordinated phosphorus compounds (Said *et al.*, 1997).



(5)

The molecular structure of (5) is shown in Fig. 1. The P—N bond length in (5) [1.609 (2) Å] is shorter than those observed in the tricoordinated aminophosphites (1) (mean 1.656 Å) and (3) [1.635 (3) Å], but is close to that observed for the aminophosphoranes (2) [1.619 (2) Å] and (4) (1.629 Å). The seven-membered phosphepin ring has a 'row-boat' conformation similar to several other phosphorus derivatives with this ring (Said *et al.*, 1996, and references therein), with O2 at the prow of the boat. Atoms P1, O1, C7 and C12 form the basal

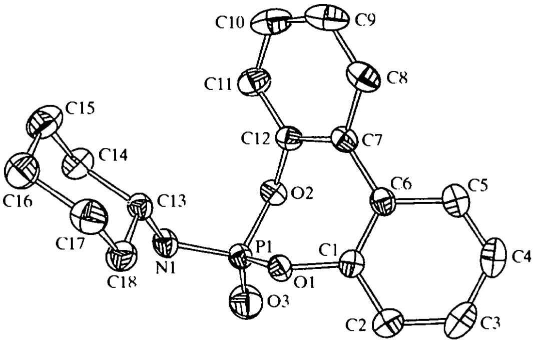


Fig. 1. The molecular structure of (5), with displacement ellipsoids plotted at the 25% probability level. For clarity, only non-H atoms are labelled.

Acta Crystallographica Section C
ISSN 0108-2701 © 1999