C2	−0.1373 (3)	0.2843 (4)	0.47678 (13)	0.0411 (7)
C3	0.0062 (3)	0.2610 (4)	0.51362 (12)	0.0398 (7)
C4	0.1387 (3)	0.1887 (4)	0.48489 (13)	0.0425 (7)
C5	0.2797 (4)	0.1658 (4)	0.51948 (15)	0.0529 (8)
C6	0.2906 (4)	0.2180 (5)	0.5846 (2)	0.0606 (9)
C7	0.1649 (4)	0.2875 (4)	0.61389 (15)	0.0576 (9)
C8	0.0176 (4)	0.3088 (4)	0.57953 (13)	0.0467 (7)
C9	−0.1201 (4)	0.3771 (4)	0.60619 (14)	0.0557 (8)
C10	−0.2570 (4)	0.3957 (5)	0.56952 (15)	0.0573 (8)
C11	−0.2681 (3)	0.3501 (4)	0.50381 (14)	0.0506 (8)
C12	−0.0239 (4)	0.1291 (5)	0.31447 (14)	0.0577 (9)
O1	0.5870 (2)	0.2011 (3)	0.84757 (9)	0.0587 (6)
O2	0.6843 (2)	0.0797 (3)	0.76138 (11)	0.0656 (7)
C13	0.5721 (3)	0.1223 (4)	0.79357 (14)	0.0476 (7)
C14	0.4064 (4)	0.0808 (5)	0.7681 (2)	0.0645 (9)
O1*W*	0.3749 (2)	0.0269 (3)	0.36254 (10)	0.0582 (6)

Table 2. *Selected geometric parameters (Å, °)*

N1—C1	1.318 (3)	C5—C6	1.406 (4)
N1—C4	1.406 (3)	C6—C7	1.360 (5)
N2—C1	1.315 (4)	C7—C8	1.410 (4)
N2—C2	1.409 (3)	C8—C9	1.417 (4)
C1—C12	1.488 (4)	C9—C10	1.356 (4)
C2—C11	1.365 (4)	C10—C11	1.405 (4)
C2—C3	1.409 (4)	O1—C13	1.265 (3)
C3—C4	1.410 (4)	O2—C13	1.238 (3)
C3—C8	1.413 (4)	C13—C14	1.504 (4)
C4—C5	1.368 (4)		
C1—N1—C4	122.8 (2)	N1—C4—C3	116.7 (2)
C1—N2—C2	122.4 (2)	C4—C5—C6	118.4 (3)
N2—C1—N1	120.9 (2)	C7—C6—C5	121.9 (3)
N2—C1—C12	119.5 (2)	C6—C7—C8	120.7 (3)
N1—C1—C12	119.5 (3)	C7—C8—C3	117.9 (3)
C11—C2—N2	121.8 (2)	C7—C8—C9	124.6 (3)
C11—C2—C3	121.2 (3)	C3—C8—C9	117.4 (3)
N2—C2—C3	117.0 (2)	C10—C9—C8	120.9 (3)
C2—C3—C4	120.1 (2)	C9—C10—C11	121.8 (3)
C2—C3—C8	120.1 (3)	C2—C11—C10	118.6 (3)
C4—C3—C8	119.9 (3)	O2—C13—O1	124.0 (3)
C5—C4—N1	122.0 (3)	O2—C13—C14	119.3 (3)
C5—C4—C3	121.2 (3)	O1—C13—C14	116.6 (3)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1*W*	0.86	1.82	2.678 (3)	173
N2—H2···O1^{i}	0.86	1.78	2.639 (3)	172
O1*W*—H1*W*···O1^{ii}	0.77	2.08	2.737 (3)	143
O1*W*—H2*W*···O2^{iii}	0.77	1.97	2.712 (3)	161

Symmetry codes: (i) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $1 - x, -y, 1 - z$.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTO*82 (Motherwell, Sussman & Beebf, 1982) and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93. Geometric calculations: *PARST* (Nardelli, 1983).

The authors thank the Council of Scientific and Industrial Research (CSIR) and the University Grants Commission (UGC), India, for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1235). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Fait, J. (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Motherwell, S., Sussman, J. L. & Beebf, N. H. F. (1982). *PLUTO*82. *Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467-473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1997). C**53**, 132–134

N,*N*′-Bis(1-pyrenylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane

Kanji Kubo,[a] Nobuo Kato[b] and Tadamitsu Sakurai[a]

[a]*Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Kanagawa-ku, Yokohama 221, Japan, and* [b]*Institute of Advanced Material Study 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816, Japan. E-mail: can@kamome.cc.kanagawa-u.ac.jp*

(*Received 23 July 1996; accepted 23 September 1996*)

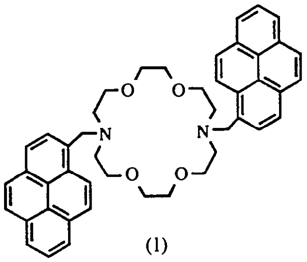
Abstract

Molecules of the title compound, $C_{46}H_{46}N_2O_4$, are centrosymmetric and the two pyrene rings are *anti* with respect to one another across the crown ether ring. No packing *via* π–π interaction between the pyrene planes is observed.

Comment

Charge-transfer (CT) molecular complexes have found wide application in the field of electronic devices as well as in chemistry. X-ray crystallographic studies of these complexes may provide direct information on the charge-transfer interaction in the ground and excited states (Winnik, 1993; Fabrizzi & Poggi, 1995; Petrov, Borisenko, Alfimov, Fiebig & Staerk, 1996). Interesting types of electron-acceptor and electron-donor molecules have recently been discovered which have aroused interest in CT complexes and their possible applications as chromoionophores and fluoroionophores (Löhr & Vögtle, 1985). It has been found that the azacrown ethers act as electron donors in a typical exciplex-forming system involving an appropriate electron acceptor (Petrov *et al.*, 1996). We have investigated the complexation behavior of the title compound, (1), with various metal ions in the excited singlet state

(Kubo & Sakurai, 1996*a*,*b*). We report here the structure of (1) with the aim of contributing to a deeper understanding of CT complex systems.



(1)

It is clear that the two pyrene units adopt an *anti* conformation with the crown ether ring. The pyrene ring of (1) is close to the N atom of the crown ether; the distance between the C1 and N1 atoms [2.505 (3) Å] is shorter than the sum of their van der Waals radii (3.05 Å). No π–π interaction is evident in the crystal packing; the distance between the pyrene planes is greater than 4.0 Å, substantially larger than that in pyrene itself (3.53 Å) (Robertson & White, 1947; Camerman & Trotter, 1965; Cohen, 1979).

The total C—C bond distance in the pyrene unit of (1) is 26.645 Å, which is close to that of pyrene itself (26.83 Å; Camerman & Trotter, 1965). The C—N1 bond lengths are not significantly shorter than the single C—N bond length [1.472 (5) Å] given by Lide (1990). This means that intramolecular charge transfer can take place readily between the pyrene unit and the N atom in (1) in the ground state as well as in the excited state.

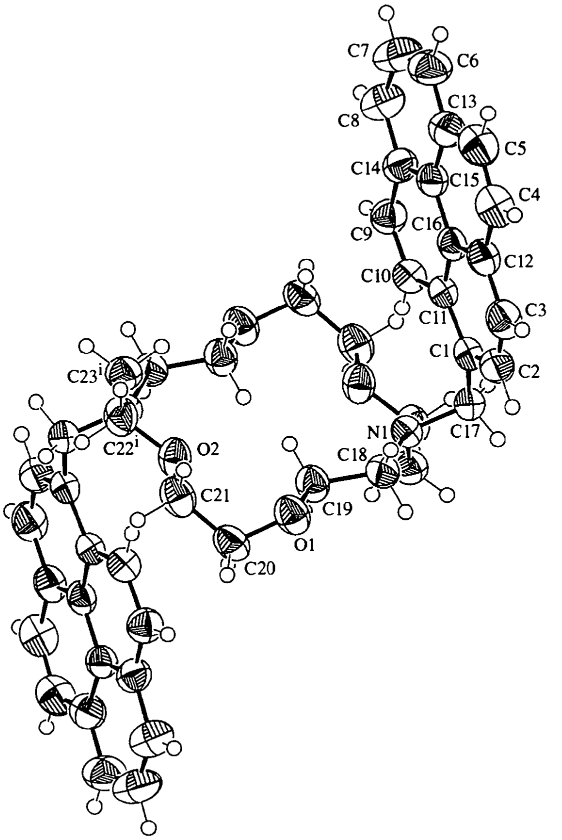


Fig. 1. The molecular structure of (1) showing 50% probability displacement ellipsoids. [Symmetry code: (i) $-x$, $1-y$, $1-z$.]

Experimental

The crystal of (1) was prepared by the condensation of 1,10-diaza-18-crown-6 with 1-pyrenylmethyl bromide (Kubo & Sakurai, 1996*a*,*b*), followed by recrystallization from chloroform.

Crystal data

$C_{46}H_{46}N_2O_4$
$M_r = 690.89$
Monoclinic
$P2_1/a$
$a = 11.503\,(2)$ Å
$b = 18.218\,(5)$ Å
$c = 9.305\,(2)$ Å
$\beta = 110.359\,(5)°$
$V = 1828.2\,(7)$ Å^3
$Z = 2$
$D_x = 1.255$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 22–42°$
$\mu = 0.627$ mm^{-1}
$T = 296\,(2)$ K
Prism
$0.35 \times 0.30 \times 0.20$ mm
Pale yellow

Data collection

Enraf–Nonius FR590 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.821$, $T_{\max} = 0.882$
3687 measured reflections
3468 independent reflections

2551 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0245$
$\theta_{\max} = 69.95°$
$h = -13 \rightarrow 14$
$k = -22 \rightarrow 0$
$l = -11 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: 0.9%

Refinement

Refinement on F^2
$R(F) = 0.0474$
$wR(F^2) = 0.1506$
$S = 1.030$
3467 reflections
235 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0734P)^2 + 0.4436P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.483$ e Å^{-3}
$\Delta\rho_{\min} = -0.149$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.07565 (12)	0.57194 (8)	0.87381 (15)	0.0621 (4)
O2	−0.14831 (12)	0.59055 (7)	0.59411 (15)	0.0595 (4)
N1	0.27300 (13)	0.48181 (8)	0.6914 (2)	0.0503 (4)

C1	0.4436 (2)	0.56885 (11)	0.6988 (2)	0.0533 (5)
C2	0.5181 (2)	0.60889 (13)	0.8237 (2)	0.0640 (5)
C3	0.5669 (2)	0.67641 (13)	0.8085 (2)	0.0650 (5)
C4	0.6041 (2)	0.77288 (12)	0.6413 (3)	0.0682 (6)
C5	0.5876 (2)	0.79812 (12)	0.5005 (3)	0.0707 (6)
C6	0.4921 (2)	0.78615 (13)	0.2185 (3)	0.0768 (6)
C7	0.4120 (3)	0.74959 (15)	0.0915 (3)	0.0872 (8)
C8	0.3493 (2)	0.68824 (13)	0.1075 (3)	0.0757 (6)
C9	0.3082 (2)	0.59389 (11)	0.2754 (2)	0.0582 (5)
C10	0.3308 (2)	0.56449 (11)	0.4161 (2)	0.0545 (5)
C11	0.4129 (2)	0.59988 (10)	0.5512 (2)	0.0478 (4)
C12	0.5456 (2)	0.70643 (11)	0.6644 (2)	0.0564 (5)
C13	0.5088 (2)	0.76172 (11)	0.3660 (3)	0.0610 (5)
C14	0.3659 (2)	0.65992 (11)	0.2540 (2)	0.0569 (5)
C15	0.4461 (2)	0.69703 (10)	0.3845 (2)	0.0516 (4)
C16	0.4667 (2)	0.66821 (10)	0.5342 (2)	0.0489 (4)
C17	0.4055 (2)	0.49140 (11)	0.7200 (2)	0.0580 (5)
C18	0.2371 (2)	0.51793 (11)	0.8095 (2)	0.0552 (5)
C19	0.0998 (2)	0.52796 (12)	0.7611 (2)	0.0586 (5)
C20	−0.0501 (2)	0.57246 (12)	0.8628 (2)	0.0640 (5)
C21	−0.1321 (2)	0.62093 (12)	0.7397 (2)	0.0645 (5)
C22	0.2343 (2)	0.37029 (11)	0.5272 (2)	0.0620 (5)
C23	0.2395 (2)	0.40389 (11)	0.6771 (2)	0.0615 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1—C20	1.414 (2)	N1—C23	1.465 (2)
O1—C19	1.422 (2)	C1—C17	1.511 (3)
O2—C22^{i}	1.408 (2)	C18—C19	1.496 (2)
O2—C21	1.414 (2)	C20—C21	1.494 (3)
N1—C18	1.459 (2)	C22—O2^{i}	1.408 (2)
N1—C17	1.464 (2)	C22—C23	1.506 (3)
C20—O1—C19	114.06 (14)	C18—N1—C23	111.77 (15)
C22^{i}—O2—C21	113.02 (15)	N1—C17—C1	114.76 (15)
C18—N1—C17—C1	−69.1 (2)	C17—N1—C18—C19	163.5 (2)
C23—N1—C17—C1	166.0 (2)	C23—N1—C18—C19	−72.1 (2)
C2—C1—C17—N1	112.8 (2)	O2^{i}—C22—C23—N1	−57.8 (2)

Symmetry code: (i) $-x, 1-y, 1-z$.

All H atoms were located at ideal positions and included in the refinement, but were restrained to ride on their bonded atoms. The isotropic displacement parameters of the H atoms were held fixed to $1.2U_{eq}$ of their riding atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Xtal GX* (Hall & du Boulay, 1995). Software used to prepare material for publication: *SHELXL*93.

This work was supported by a Grant-in-Aid for Encouragement of Young Scientists from the Ministry of Education, Science and Culture, Japan (08740554).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, M. C., Cascarano, C., Giacovazzo, A., Guagliardi, G., Burla, M., Polidori, J. & Camalli, G. (1994). *J. Appl. Cryst.* **27**, 435–436.

Camerman, A. & Trotter, J. (1965). *Acta Cryst.* **18**, 636–643.

Cohen, M. D. (1979). *Mol. Cryst. Liq. Cryst.* **50**, 1–10.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fabrizzi, L. & Poggi, A. (1995). *Chem. Soc. Rev.* pp. 197–202.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Hall, S. R. & du Boulay, D. (1995). *Xtal GX*. University of Western Australia, Australia.

Kubo, K. & Sakurai, T. (1996*a*). *Chem. Lett.* Submitted.

Kubo, K. & Sakurai, T. (1996*b*). *Rep. Inst. Adv. Mater. Study Kyushu Univ.* **10**. In the press.

Lide, R. D. (1990). In *Handbook of Chemistry and Physics*, 71st ed. Boston: CRC Press.

Löhr, H. G. & Vögtle, F. (1985). *Acc. Chem. Res.* **18**, 65–72.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Petrov, N. K., Borisenko, V. N., Alfimov, M. V., Fiebig, T. & Staerk, H. (1996). *J. Phys. Chem.* **100**, 6368–6370.

Robertson, J. M. & White, J. G. (1947). *J. Chem. Soc.* pp. 358–368.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Winnik, F. M. (1993). *Chem. Rev.* **93**, 587–614.

Acta Cryst. (1997). C**53**, 134-136

L-Histidinol Phosphate Tetrahydrate

Tamami Suga and Nobuo Okabe

Faculty of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashiosaka, Osaka 577, Japan

(*Received 28 May 1996; accepted 7 October 1996*)

Abstract

In the crystal structure of the title compound, $C_6H_{12}N_3O_4P.4H_2O$, the amino group is protonated by the phosphate group. The phosphate group is *trans* planar to the central asymmetric C atom and projects out the plane of the imidazole ring. The crystal structure is stabilized by a three-dimensional network of all possible hydrogen bonds.

Comment

L-Histidinol phosphate is an intermediate in histidine biosynthesis (Ames & Mitchell, 1955; Ames & Horecker, 1956). It is derived enzymatically from imidazoleacetate phosphate catalyzed by imidazole-acetol phosphate transaminase and further converted to histidinol by histidinol phosphate aminotransferase (Martin & Goldberger, 1967; Henderson & Snell, 1973). Recently, the homology of aspartate, tyrosine and histidinol phosphate aminotransferases has been reported from the investigation on evolutionary relationships among vitamine B_6-dependent aminotransferases (Metha, Hale & Christen, 1989, 1993). It is important, therefore, to determine the fine structure of the substrate for these transferases in order to elucidate the structural mechanism of the enzymatic action.

Acta Crystallographica Section C
ISSN 0108-2701 © 1997