STRUCTURE OF *bis* (2,2'-BIPYRIDYL)*bis* (2,4,6-TRINITROPHENOLATO)-CALCIUM(II) [$Ca(C_{10}N_2H_8)_2\ (C_6N_3O_7H_2)_2$]

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ABSTRACT

[Ca $(C_{10}N_2H_8)_2$ $(C_6N_3O_7H_2)_2$], $M_y = 808.7$, m.p. = 488–498 K, orthorhombic, *Pbca*, $a = 24.154(5)$, $b = 16.128(5)$, $c = 18.068(6)$ Å, $v = 7038.5$ Å^3, $Z = 8$, $D_c = 1.528$, $D_m = 1.532$ g cm (flotation), λ (Mo K_α) = 0.7107 Å, Zr filter, $\mu = 2.53$ cm^{-1}, $F(000) = 3312$, room temperature, $R = 0.068$ for 1263 observed reflections. Calcium is eight-coordinated to the four N atoms of 2,2'-bipyridines (bipy) and to the four O atoms belonging to the two trinitrophenolates (tnp) in a distorted square antiprism geometry. In the coordination polyhedra, distances between Ca and phenolic O atoms are shorter than the other Ca–O and Ca–N bond distances. The nitro groups are rotated out of the ring planes of tnp. In both bipy molecules the rings are in the twisted conformation.

INTRODUCTION

IN continuation of our studies on the coordination properties of alkali and alkaline earth cations with respect to various ligands (particularly with the coordinating capacity of nitrophenols[1–3]), crystal structure determination of the title compound was undertaken.

EXPERIMENTAL

Crystals prepared by mixing calcium trinitrophenolate and 2,2'-bipyridine in 1:1 ratio in a solvent with equal amounts of acetone and ethanol; slow evaporation at room temperature yields yellow crystals. Intensity data (crystal size $0.56 \times 0.25 \times 0.73$ mm^3) collected using indigenously fabricated computer-controlled four-circle diffractometer, Zr-filtered Mo K_α radiation, ω-2θ step scan, 3889 reflections recorded in the range $3 \leqslant 2\theta \leqslant 42°$, 1263 with $I > 2.5\,\sigma(I)$ considered observed, index range h 0→22, k 0→16, l 0→16. Corrections applied for Lp and absorption, maximum and minimum values of absorption 0.939 and 0.834 respectively. Cell parameters from least-squares refinement of setting angles of 25 reflections (θ range 8–15°), two check reflections for every 100 data reflections did not vary significantly over the course of data collection, Patterson and Fourier methods, all hydrogens located from difference maps, structure refinement by least-squares based on F values with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms. $R = 0.067$, $Rw = 0.097$ with $w = 0.5641/[\sigma^2(F) + 0.01058\,F^2]$; $\Delta/\sigma(\max) = 0.63$; $\Delta\rho$ in final difference map -0.3 to $0.4\,e$ Å^{-3}, C–H distances in the range 0.916(16) to 1.224(14) Å, e.s.d. are found to be large, may be due to poor ratio of observation to the number of variables (non-hydrogen 513 variables; hydrogens 80 variables); programs SHELX-76[4], PLUTO[5]; computer NORSK DATA; atomic scattering factors those from SHELX-76.

DISCUSSION

The final positional parameters are given in table 1. The molecular structure of the compound is shown in figure 1. The Ca atom is eight-coordinated by four N atoms of the two bidentate bipy ligands, two O atoms of the phenolic and two O atoms of the *o*-nitro group of the two tnp moieties (figure 2). The symmetry of the coordination polyhedra was examined by the Lippard and Russ[6] test. The angle between intersecting trapezoidal best planes for the polyhedra was 85.4°(9). On these grounds the coordination is an intermediate case between the ideal square antiprism (77.4°) and the ideal dodecahedron (90°). The additional test based on the comparison of average distance of the ligand atoms to

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Table 1 *Final atomic coordinates (× 10⁴) and equivalent temperature factors (Å² × 10³) with e.s.d.*

	x	y	z	U_{eq}
Ca (1)	1781 (1)	665 (2)	2633 (2)	42 (3)
(tnp1)				
O (2)	1438 (4)	51 (6)	1585 (5)	54 (6)
C (3)	1025 (7)	−360 (9)	1362 (9)	51 (8)
C (4)	923 (6)	−484 (8)	580 (8)	42 (7)
N (5)	1356 (5)	−270 (9)	14 (8)	56 (7)
O (6)	1826 (5)	−408 (8)	209 (6)	93 (7)
O (7)	1179 (5)	15 (8)	−567 (7)	85 (7)
C (8)	440 (7)	−874 (9)	271 (8)	53 (7)
C (9)	42 (6)	−1161 (9)	801 (9)	48 (7)
N (10)	−467 (6)	−1590 (9)	521 (9)	71 (8)
O (11)	−523 (5)	−1626 (9)	−149 (8)	110 (7)
O (12)	−769 (5)	−1887 (7)	977 (7)	75 (7)
C (13)	85 (6)	−1049 (9)	1561 (9)	52 (8)
C (14)	573 (6)	−666 (11)	1799 (8)	56 (8)
N (15)	602 (5)	−548 (9)	2627 (8)	66 (7)
O (16)	1063 (4)	−469 (7)	2921 (6)	63 (6)
O (17)	173 (5)	−556 (8)	2963 (6)	89 (7)
(tnp2)				
O (2′)	898 (3)	1278 (7)	2646 (5)	53 (5)
C (3′)	487 (6)	1398 (10)	3070 (9)	51 (6)
C (4′)	478 (6)	1285 (9)	3878 (9)	47 (7)
N (5′)	984 (6)	965 (8)	4224 (8)	61 (7)
O (6′)	1450 (4)	1013 (7)	3907 (6)	65 (6)
O (7′)	942 (6)	686 (9)	4857 (7)	106 (7)
C (8′)	−40 (6)	1432 (9)	4344 (7)	45 (7)
C (9′)	−447 (6)	1713 (8)	4019 (9)	52 (7)
N (10′)	−892 (6)	1938 (10)	4496 (9)	80 (9)
O (11′)	−1305 (5)	2308 (8)	4336 (7)	96 (7)
O (12′)	−900 (6)	1748 (9)	5127 (8)	121 (8)
C (13′)	−487 (7)	1876 (10)	3301 (10)	65 (8)
C (14′)	−62 (8)	1673 (10)	2845 (10)	70 (8)
N (15′)	−84 (7)	1841 (12)	2025 (11)	89 (8)
O (16′)	−193 (7)	1229 (11)	1668 (8)	141 (10)
O (17′)	−29 (8)	2475 (11)	1782 (9)	179 (10)
(bipy1)				
N (18)	2661 (5)	80 (8)	2057 (6)	42 (6)
C (19)	2829 (7)	382 (10)	1409 (8)	53 (7)
C (20)	3401 (8)	302 (10)	1153 (9)	69 (8)
C (21)	3761 (7)	−169 (12)	1627 (10)	72 (9)
C (22)	3562 (7)	−463 (11)	2285 (9)	70 (9)
C (23)	3021 (6)	−364 (10)	2513 (10)	55 (8)
C (24)	2800 (5)	−732 (9)	3178 (7)	35 (7)
N (25)	2313 (5)	−388 (7)	3439 (7)	54 (8)
C (26)	2106 (7)	−701 (10)	4071 (8)	59 (9)
C (27)	2359 (7)	−1356 (11)	4455 (8)	65 (9)
C (28)	2833 (7)	−1699 (10)	4145 (9)	68 (9)
C (29)	3076 (7)	−1392 (11)	3529 (8)	65 (9)
(bipy2)				
N (18′)	2568 (5)	1637 (7)	2995 (6)	47 (8)
C (19′)	2921 (6)	1485 (10)	3594 (9)	62 (7)
C (20′)	3364 (6)	1977 (11)	3759 (8)	50 (6)
C (21′)	3526 (6)	2598 (12)	3319 (9)	60 (7)
C (22′)	3187 (6)	2715 (9)	2702 (7)	44 (6)
C (23′)	2724 (7)	2277 (9)	2530 (9)	57 (6)
C (24′)	2367 (6)	2413 (10)	1862 (8)	42 (6)
N (25′)	1924 (5)	1909 (8)	1838 (6)	51 (7)
C (26′)	1558 (7)	2072 (9)	1258 (9)	60 (7)
C (27′)	1623 (7)	2665 (11)	789 (9)	63 (7)
C (28′)	2083 (7)	3201 (10)	806 (8)	63 (7)
C (29′)	2472 (7)	3025 (9)	1383 (8)	54 (6)

$U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

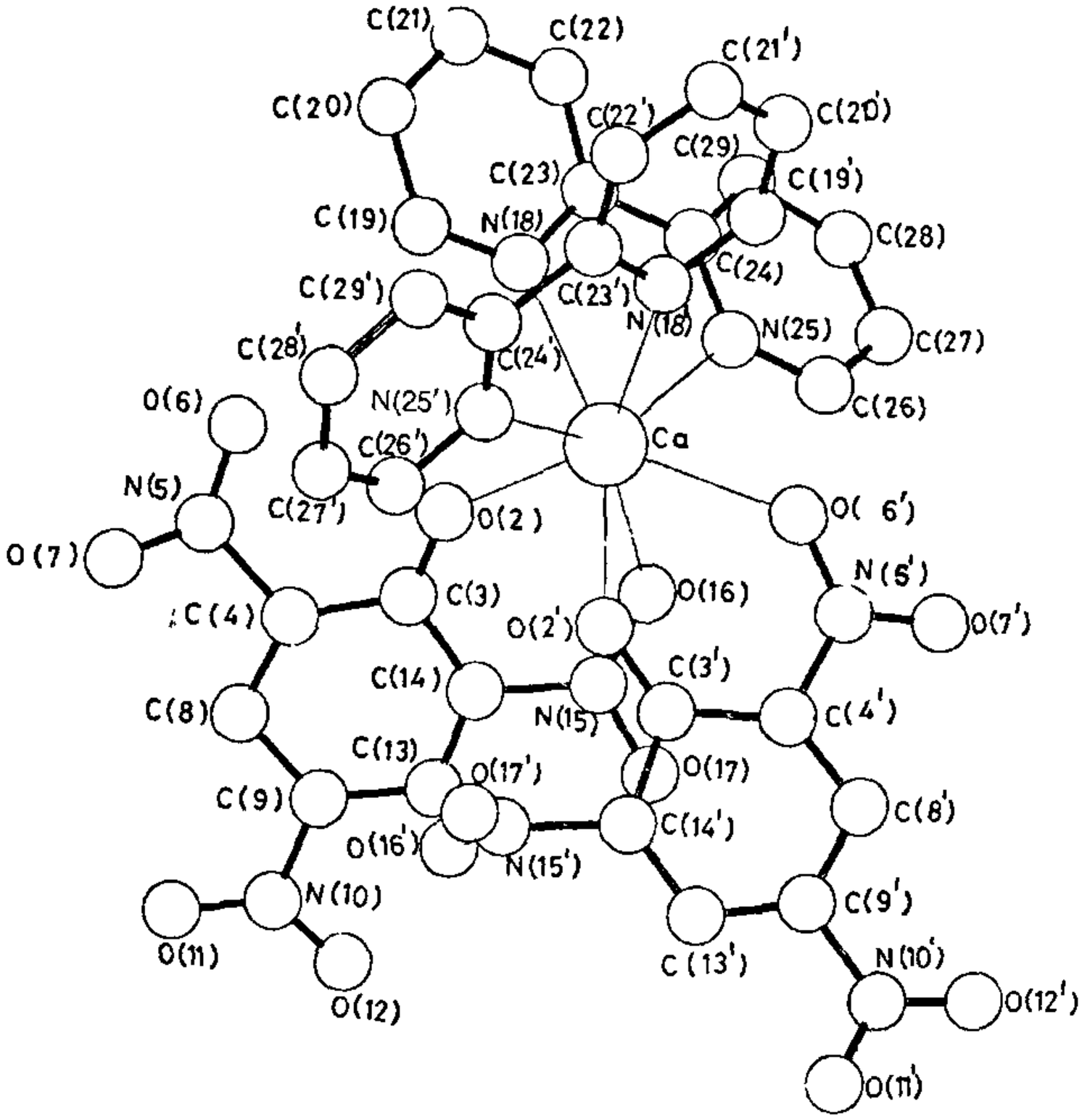

Figure 1. Molecular structure of *bis*(2,2'-bipyridyl)*bis*(2,4,6-trinitrophenolato)calcium(II).

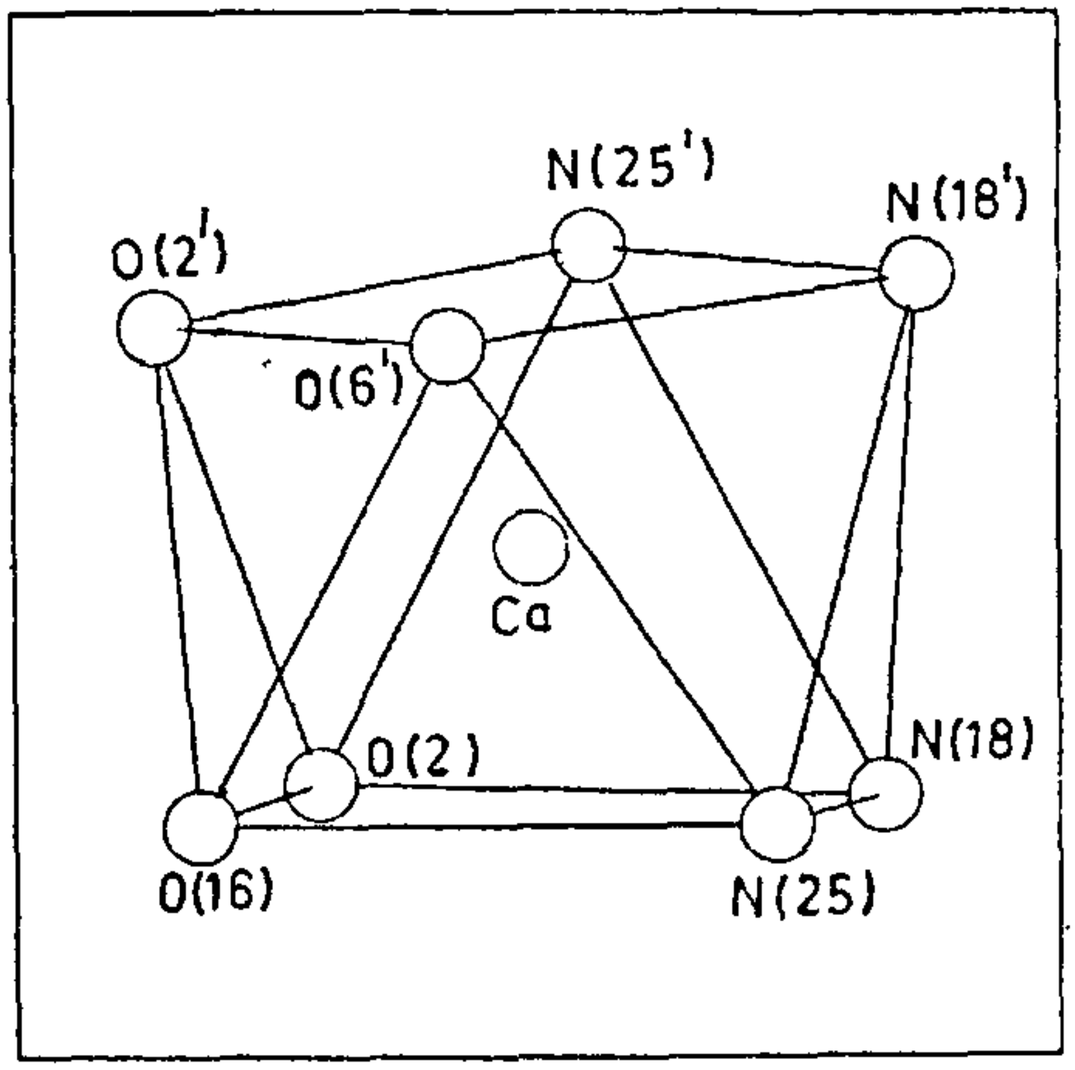

Figure 2. Calcium coordination in *bis*(2,2'-bipyridyl)-*bis*(2,4,6-trinitrophenolato)calcium(II).

trapezoidal planes [dT=0.275(15), dT=0.314(14) Å] with average distance of the ligand atoms to the best planes through the square faces of the antiprism [dS = 0.19(8), dS = 0.023(9) Å] allows us to describe the polyhedra as distorted square antiprisms. Table 2 gives bond lengths and bond angles. The distances between Ca and phenolic O(2) and O(18) atoms [2.292(10), 2.351(9) Å] are smaller than the other Ca–O and Ca–N distances, which lie in the range 2.492(12)–2.578(12) Å. Calcium displays two properties, viz. anionphilicity by virtue of which it interacts strongly with the phenoxide and a strong polarizing ability towards the neutral N atoms of bipy compared to O atoms of NO group of tnp. The O–Ca–O bite angles of tnp [66.8(3), 67.5°(3)] are observed to be greater than the bite angles N–Ca–N of bipy [64.6(4) and 63.2°(4)]. The bond lengths and angles of the benzene ring of the two tnp's agree with those reported in many nitrophenolate complexes[7–9] and show common features such as larger C–C bond lengths and smaller C–C–C angles at the

Table 2 *Bond lengths (Å) and angles (degrees) with e.s.d.*

Ca (1)–O (2)	2.292 (10)	O (2) O (16)	2.712 (12)
Ca (1)–O (2′)	2 351 (9)	O (16) N (25)	3.164 (13)
Ca (1)–O (16)	2.574 (11)	N (25)–N (18)	2.741 (13)
Ca (1)– O (6′)	2.502 (10)	N (18)–O (2)	3 075 (14)
Ca (1)–N (18)	2.547 (11)	O (2′)–O (6′)	2.675 (14)
Ca (1)–N (25)	2.579 (12)	O (6′)–N (18′)	3.321 (14)
Ca (1)–N (18′)	2.550 (12)	N (18′)– N (25′)	2.643 (13)
Ca (1)–N (25′)	2.492 (12)	N (25′)–O (2′)	3.050 (13)
	(tnp1)	(tnp2)	
O (2)–C (3)	1.265 (18)	1.270 (17)	
C (3)–C (4)	1.448 (21)	1 472 (23)	
C (4)–C (8)	1.439 (21)	1.372 (20)	
C (8)–C (9)	1.433 (20)	1.392 (21)	
C (9)–C (13)	1.388 (21)	1.327 (24)	
C (13)–C (14)	1.398 (20)	1.356 (25)	
C (14)–C (3)	1.435 (21)	1.457 (23)	
C (4)–N (5)	1 502 (19)	1.467 (20)	
C (9)–C (10)	1.499 (20)	1.425 (22)	
C (14)–N (15)	1.511 (20)	1.507 (26)	
N (5)–O (6)	1.211 (17)	1.266 (17)	
N (5)–O (7)	1.223 (18)	1.233 (18)	
N (10)–O (11)	1.218 (20)	1.258 (19)	
N (10)–O (12)	1.201 (20)	1.181 (20)	
N (15)–O (16)	1.239 (16)	1.209 (25)	
N (15)–O (17)	1.202 (18)	1.121 (27)	
	(bipy1)	(bipy2)	
N (18)–C (19)	1.332 (18)	1.400 (19)	
C (19)–C (20)	1.463 (23)	1.365 (21)	
C (20)–C (21)	1.437 (24)	1.337 (23)	
C (21)–C (22)	1.369 (24)	1.397 (21)	
C (22)–C (23)	1.378 (22)	1.359 (21)	
C (23)–N (18)	1.395 (19)	1.383 (19)	
C (23)–C (24)	1.444 (21)	1.499 (21)	
C (24)–N (25)	1.382 (18)	1.344 (18)	
N (25)–C (26)	1.345 (19)	1.395 (20)	
C (26)–C (27)	1.403 (23)	1.287 (22)	
C (27)–C (28)	1.390 (23)	1.408 (23)	
C (28)–C (29)	1.352 (22)	1.433 (22)	
C (29)–C (24)	1.408 (21)	1.336 (20)	
O (2)–Ca (1)–O (16)	67.5 (3)	O (2)–O (16)–N (25)	86.2 (6)
N (18)–Ca (1)–N (25)	64.6 (4)	O (16)–N (25)–N (18)	92.1 (8)
O (2′)–Ca (1)–O(6′)	66.8 (3)	N (25)–N (18)–O (2)	87.3 (8)
N (18′)–Ca (1)–N (25′)	63.2 (4)	N (18)–O (2)–O (16)	94.5 (6)
O (2)–Ca (1)–O (2′)	82.1 (3)	O (2′)–O (6′)–N (18′)	86.2 (6)
O(2′)–Ca(1)–O(16)	71.7(3)	O(6′)–N(18′)–N(25′)	87.9 (8)
O (16)–Ca (1)–O (6′)	76.0(3)	N(18′)–N(25′)–O (2′)	92.6 (6)
O (6′)–Ca (1)–N (25)	77.7(4)	N(25′)–O(2′)–O(6′)	93.0 (6)
N (25)–Ca (1)–N (18′)	83.6 (4)		
N (18′)–Ca (1)–N (18)	73.2 (4)		
N (18)–Ca (1)–N (25′)	87.0 (4)		
N (25′)–Ca (1)–O (2)	85.5 (4)		
	(tnp1)	(tnp2)	
O (2)–C (3)–C (4)	111.1 (13)	126.3 (13)	
C (3)–C (4)–C (5)	121.0 (13)	117.0 (13)	
C (4)–N (5)–O (6)	115.3 (12)	121.8 (12)	
C (4)–N (5)–O (7)	114.3 (13)	117.2 (13)	
O (6)–N (5)–O (7)	130.3 (14)	120.9 (14)	
N (5)–C (4)–C (8)	113.6 (12)	116.2 (14)	
C (3)–C (4)–C (8)	125.2 (13)	126 8 (13)	
C (4)–C (8)–C (9)	115.3 (12)	116.6 (13)	
C (8)–C (9)–N (10)	118.2 (13)	117.7 (14)	

Table 2. (*Contd.*)

C (9)–N (10)- O (11)	116.6 (14)	118.8 (15)
C (9)–N (10)–O (12)	116.8 (14)	122.1 (15)
O (11)–N (10)–O (12)	126.5 (15)	118.8 (15)
N (10)–C (9)–C (13)	117.1 (13)	119.1 (14)
C (8)–C (9)–C (13)	124.6 (13)	122.6 (15)
C (9)–C (13)–C (14)	115.1 (12)	119.3 (16)
C (13)–C (14)–N (15)	113.6 (12)	121.8 (15)
C (14)–N (15)–O (16)	118.7 (12)	112.6 (16)
C (14)–N (15)- O (17)	117.2 (12)	123.1 (18)
O (16)–N (15)–O (17)	124 0 (14)	124.2 (20)
N (15)–C (14)–C (3)	117.7 (13)	111.1 (14)
C (13)–C (14)–C (3)	128.6 (14)	126.5 (16)
C(14)–C(3)–C(4)	127.3 (14)	107.5 (13)
C (14)–C (3)–O (2)	127.3 (14)	126.2 (14)
	(bipy1)	(bipy2)
N (18)–C (19)–C (20)	122.2 (13)	105.8 (12)
C (19)–C (20)–C (21)	115.4 (14)	122.4 (14)
C (20)–C (21)–C (22)	119.3 (15)	113.8 (14)
C (21)–C (22)–C (23)	123.4 (16)	126.6 (14)
C (22)–C (23)–N (18)	118.3 (14)	118.2 (14)
C (23)–N (18)–C (19)	121.2 (12)	115.8 (12)
C (22)–C (23)–C (24)	123.5 (14)	125.6 (14)
N (18)–C (23)–C (24)	118.1 (12)	116.3 (13)
C (23)–C (24)–N (25)	123.6 (12)	113.3 (12)
C (24)–N (25)–C (26)	117.1 (12)	114.5 (12)
N (25)–C (26)–C (27)	126.6 (14)	123.8 (15)
C (26)–C (27)–C (28)	117.4 (14)	122.6 (15)
C (27)–C (28)–C (29)	122.9 (15)	114.3 (14)
C (28)–C (29)–C (24)	116.2 (14)	119.5 (15)
C (29)–C (24)–N (25)	123.6 (12)	125.2 (13)
C (29)–C (24)–C (23)	120.7 (12)	121.3 (13)

phenolic sites, and enlarged angles (126°) at *ortho* C atoms. The phenyl rings are moderately planar, the σ_{plane}, defined as $[\sum_i d_i^2 /(n-3)^{1/2}]$, where d is the distance of atom from plane and n is the number of atoms in the plane, being 0.006(6) and 0.026(8) Å. The nitrogens (ring substitutions) show more deviations from the least-squares plane in tnp1 [N(5), 0.12(1); N(10), 0.06; N(15), −0.04(1) Å] than in tnp2 [N(5'), 0.01(1); N(10'), 0.10(1); N(15'), 0.00(1) Å]. Apart from bending relative to the plane of the benzene ring, the planes of the nitro group display various degrees of twisting—moderate for *para* nitro groups and large for *ortho* nitro groups [in tnp1 7.2(7), 39.4(8), 23.6°(8); in tnp2 10.7(1), 18.5(8), 83.8°(8)], 83.8° being the largest twist reported so far. The two tnp planes are inclined at 55.9°(8) to each other. Tables of mean planes, torsional angles and F_o, F_c are available from the authors. In the two bipys, the intraligand twist angle (based on parameters defined by Cordes *et al.*[10]) were found to be 19.4(7) and 5.4°(7), and χ_c values were found to be 3.4 and 1.4°. This suggests that in both the bipys the rings are in the twisted conformation and not in the bowed conformation. The packing of the molecules shows no abnormally short contacts.

29 June 1988; Revised 17 June 1989

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ANNOUNCEMENTS

New Drug Strategies in the Prevention and Treatment of Stroke

Date: 24–25 January 1990
Place: London

Stroke occurs commonly and with devastating consequences. Patients are often left dependent on expensive nursing care, and in need of years of rehabilitation therapy. Is there not more that can be done to prevent stroke or to minimise the damage it wreaks?

This international conference will examine drug strategies that have been tried in the past, and novel pharmacological approaches currently under study, in both the prevention and the treatment of acute stroke. Experts in the field will discuss the latest developments, reviewing results from large clinical studies and examining the progress that is being made on the experimental front. The meeting, aimed specifically at all those involved in testing and developing new drugs for use in stroke, will provide an invaluable overview of present day management of the condition, and changes that the future may bring.

Osteoporosis—Prospects for Prevention and Treatment

Date: 5–6 October 1990
Place: London

The objective of this meeting is to bring together leading authorities, to discuss basic research and clinical studies related to osteoporosis. Oestrogens play a central role in preventing bone loss. The role of hormone replacement therapy in postmenopausal women and its associated risks and benefits will be discussed. The strategies and techniques available for screening and designing trials will also be discussed. For the future, there is a strong need to develop new pharmacological agents that will stimulate new bone formation and enhance bone mass. The new leads in this direction will be reviewed, as well as experimental approaches for their evaluation.

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