T. E. Sloan and J. E. Blackwood of Chemical Abstracts for assistance on the nomenclature and stereochemical notations for these compounds.

Registry No. 6**a**, 91604-85-2; **6b**/$\bar{6}$**b**, 91550-90-2; **6c**/$\bar{6}$**c**, 91550-91-3; **6d**/$\bar{6}$**d**, 91550-92-4; **6e**/$\bar{6}$**e**, 91604-86-3; **6f**/$\bar{6}$**f**, 91604-87-4; **7a**, 89173-06-8; **7b**, 91604-88-5; **7c**, 91604-89-6; **7d**, 91604-90-9; *dl*-**10**, 91550-93-5; *dl*-**13**, 88496-14-4; *dl*-**14**, 88496-13-3; *dl*-**19**, 82762-43-4; *dl*-**27**, 82762-42-3; $Cl(CH_2)_3Cl$, 142-28-9; $PhPH_2$, 638-21-1; Na_2PdCl_4, 13820-53-6; 1-chloro-3-(dicyclohexylphosphino)propane, 71734-57-1; dicyclohexylphosphine, 829-84-5; lithium dicyclohexylphosphide, 19966-81-5; dichloro(1,5-cyclooctadiene)platinum(II), 12080-32-9; dimethyl(1,5-cyclooctadiene)platinum(II), 12266-92-1; $\bar{6}$**a**, 91604-91-0.

Supplementary Material Available: Additional bond lengths and bond angles for **7a** and **6a**, selected torsion angles for **7a**, **6a**, and **6f**, least-squares planes for the platinum coordination spheres, positional and thermal parameters for **7a**, **6a**, and **6f**, and a listing of observed and calculated structure factors (64 pages). Ordering information is given on any current masthead page.

Conformations of the Nonbonded and the Coordinated Ligand Nonamethylimidodiphosphoramide (NIPA) in the Solid State and in Solution. X-ray Structure Determinations, NMR Study, and Theoretical Calculations on the NIPA Molecule and the Complex $[UO_2(NIPA)_2C_2H_5OH](ClO_4)_2$

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Abstract: The structures of crystalline nonamethylimidodiphosphoramide (NIPA) and its uranyl complex $[UO_2(NIPA)_2C_2H_5OH](ClO_4)_2$ (B) as determined by X-ray diffraction are compared to results from NMR spectroscopy on solutions. It is shown that in solid NIPA the P═O groups are in a "trans" conformation whereas in polar solvents (CH_2Cl_2, CH_3NO_2) and in the complex they are in a "cis" arrangement. The total energies of the two conformations were calculated theoretically by the CNDO/2 method and a stabilization of ca. 10 kJ mol^{-1} was found for the "cis" conformation of NIPA when surrounded by a polar solvent. ^{31}P–^{31}P and ^{31}P–^{15}N coupling constants were equally calculated and agree well with the values of $|^2J_{P-P}{}^{cis}|$ (15.6 Hz), $|^2J_{P-P}{}^{trans}|$ (22.0 Hz), and $|^1J_{P-N}{}^{cis}|$ (33.4 Hz) determined experimentally.

Phosphorylated molecules (i.e., containing the ⋗P═O group) are very good ligands for many metallic ions and are therefore often used as extractants in liquid–liquid extraction processes,[2] especially for the uranyl cation $UO_2{}^{2+}$.

It has been reported previously[3] that the β-biphosphorylated chelating compound nonamethylimidodiphosphoramide (NIPA, $[(Me_2N)_2P(:O)]_2NMe$) forms a stable complex with uranyl perchlorate.

Recently we showed that, depending on the method of preparation, complexes of different stoichiometries are formed between NIPA and the $UO_2{}^{2+}$ ion:[4-6] $[UO_2(NIPA)_3]^{2+}$, $2ClO_4{}^-$ (A); $[UO_2(NIPA)_2S]^{2+}$,$2ClO_4$, S = H_2O, CH_3OH, C_2H_5OH (B), and $(CH_3)_2CO$; $[(UO_2)_2(NIPA)_5]^{4+}$,$4ClO_4{}^-$ (C).

The knowledge of the structures of the complexes in the solid state and in solution is particularly important for the better understanding of the exceptional coordinating ability of this class of neutral bidentate ligands.

From the ^{31}P NMR spectra of solutions of the complexes in a 2:1 v/v dichloromethane–nitromethane mixture (called C_2N in the following) it was possible to infer the ligand arrangement around the uranyl ion. In all of these complexes the coordination number of uranium is seven, the oxygen atoms of the ligand being located in a plane perpendicular to the linear O═U═O unit.

In complex A two ligand molecules are bidentate whereas the third one is bound to the ion by only one P═O group. Both molecules of NIPA in complex B are bidentate, the fifth coordination site in the equatorial plane being occupied by the oxygen atom of ligand S. Complex C, which has not been isolated in the solid state, exists in equilibrium with complexes A and B in solution. Its peculiar structure may be represented as two $[UO_2(NIPA)_2]^{2+}$ units containing bidentate NIPA ligands, connected by a bridging NIPA molecule.

All these results suggested that coordinated NIPA can assume different geometries. In the bidentate molecule the two P═O groups are obviously in a "cis" conformation; in the case of the monodentate NIPA in complex A or of the bridging NIPA in complex C they should be in a "trans" conformation for steric reasons.

This assumption is corroborated by the observation of different NMR coupling constants $|^2J_{P-P}|$ for the bidentate (15.6 Hz) and the monodentate molecule (22.0 Hz).

Only crystals of complex B were available for crystallographic studies, A yielding merely oily products in a variety of solvents tried for recrystallization.

If the coordinated ligand can adopt different conformations in its complexes, the same may be true for free NIPA. Therefore,

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Table I. Experimental Data and Refinement Parameters

	NIPA	Complex B
cryst system	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1mn$
a, Å	6.866 (3)	8.407 (4)
b, Å	13.612 (2)	15.464 (3)
c, Å	17.818 (2)	18.365 (3)
β, deg	101.65 (3)	
V, Å^3	1631	2387
Z	4	2
ρ_{calcd}, g cm^{-3}	1.25	1.50
cryst dimens	0.3 × 0.3 × 0.5 mm^3	0.46 × 0.17 × 0.11 mm^3
diffractometer	CAD4-F Enraf Nonius	CAD4-Enraf Nonius
radiation	Ag Kα (λ = 0.559 36 Å)	Mo Kα (λ = 0.709 26 Å)
scan procedure	(θ, 2θ)	(θ, 2θ)
θ range	$1° < \theta < 25°$	$0 < \theta < 30°$
unique reflcns collecd	4669	3871
unique reflcns in refinement	2367 ($I > 3\sigma(I)$)	2104 ($I > 3\sigma(I)$)
ref reflcns	4, every 2 h (no decay)	3, every 2 h (30% decay)
checking of the cryst alignment	every 100 reflectns (~8 h)	every 50 reflectns
corrections	Lorentz and polarization, no absorption correction ($\mu R < 0.1$)	Lorentz and polarization, numerical absorption corrections ($0.55 < T < 0.68$)
R_F, R_{wF},[a] %	4%, 4%	6.2%, 6%

[a] For explanations see the text.

in the present paper, in addition to the crystallographic study of complex B, the structure of solid NIPA has been determined by X-ray diffractometry.

Moreover, the conformation of NIPA in C_2N solution has been elucidated by measuring the coupling constant $|^2J_{P-P}|$ from the ^{31}P and ^{15}N NMR spectra.

In order to confirm the results a theroretical study of the relative energies of the different conformations for an isolated molecule and for NIPA in a polar medium has been undertaken.

Experimental Section

Materials. NIPA and complex B have been synthetized by a method described earlier.[7] NIPA was recrystallized from petroleum ether and complex B from absolute ethanol. C.E.A. deuterated nitromethane and Prolabo "normapur" grade dichloromethane were used as solvents after dehydration over molecular sieves. All manipulations were carried out under purified argon in a glovebox because of the hygroscopic character of NIPA and its complexes. The crystals of NIPA and complex B were sealed in Lindeman glass capillaries for the crystallographic studies.

Although no specific indications about the toxicity of NIPA and its compounds are found in the literature, precautions were taken in handling this substance because of its close resemblance to OMPA (octamethylpyrophosphoramide).[22]

NMR Spectroscopy. ^{31}P and ^{15}N NMR spectra were taken on a Bruker WP 80 spectrometer at 32.44 and 8.10 MHz, respectively, with CD_3NO_2 as internal lock substance. The $^{31}P\{^1H\}$ spectrum was recorded at −48.5 °C (0.573 mol NIPA/kg C_2N) on a degassed sample tube (5-mm diameter). The observed sidebands were very small compared to the main signal (about 1:1000 for the smallest ones), and in order to obtain a good signal to noise ratio at least 4500 scans were necessary. The width of the signals was reduced by Gaussian multiplication of the Free Induction Decay. The $^{15}N\{^1H\}$ spectrum was obtained at room temperature after 13 000 scans with a solution of 5.864 mol NIPA/kg C_2N in a 10-mm tube.

Crystallographic Measurements. The data of the crystals as well as the experimental and refinement parameters are given in Table I.

NIPA. The crystal of NIPA was a parallelepiped elongated along the [100] crystallographic axis. Weissenberg photographs revealed a lattice symmetry $2/m$ and systematic absences $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$) defining uniquely the monoclinic space group $P2_1/c$. Preliminary cell dimensions were measured from Weissenberg photographs and a $h0l$ precession photograph then adjusted by a least-squares procedure applied to the setting angles of 25 reflections measured on a CAD4-F Enraf Nonius diffractometer using Ag Kα radiation.

Complex B. Investigations by Weissenberg photographs showed the crystal system to be orthorhombic with systematic absences $hk0$ ($h + k = 2n + 1$) in agreement with the space groups $Pmmn$, $Pm2_1n$, and $P2_1mn$. During the examination under the binocular microscope in the glovebox, we noticed the aggregation of crystals under intense light. A pyroelectric effect could explain this observation. In this case the space group will be one of the two noncentrosymmetric groups $Pm2_1n$ or $P2_1mn$. The structure solution confirmed the latter. Intensity data were collected on the CAD4-F Enraf Nonius diffractometer with graphite-monochromated Mo Kα radiation at room temperature. The alignment of the crystal was checked every 50 reflections, and three standard reflections were measured every 2 h to monitor the crystal stability. The three standards decreased linearly by about 30% during the data collection so a correction was applied to the data. Numerical absorption corrections were calculated ($0.55 < T < 0.68$) by using the program SHELX.[8]

Solution and Refinement of the Structures

NIPA. The crystal structure was solved by direct methods using the MULTAN computer program[9] and by Fourier synthesis giving the positions of all P, O, N, and C atoms of the molecule. After several steps of anisotropic refinement all the H atoms could be detected in difference Fourier maps. In a final full-matrix least-squares refinement including a weighting scheme ($w = 1.849/[\sigma^2(F) + 0.00048F^2]$) convergence was reached at $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.040$ and $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o| = 0.040$. Isotropic temperature factors were given for the H atoms. Atomic scattering factors were taken from International Tables for X-ray Crystallography[10] and corrected for anomalous dispersion.[11] Final positional and anisotropic thermal parameters for the nonhydrogen atoms were given in Table II; positional and isotropic thermal parameters of hydrogen atoms as well as a list of calculated and observed structure factors are available as supplementary material.[12]

Complex B. Assuming a noncentrosymmetric group, the atom U lies on the mirror plane m and its coordinates will be 0, 0, z because the coordinate along the 2_1 axis is arbitrary. A Patterson function was calculated and the atom U positioned. The presence of the unique atom U in the structure introduces a supplementary mirror plane in the Fourier synthesis so that all peaks are doubled. The choice of the peaks is achieved in a way such that the atom U has the expected coordination. The space group is then unambiguously $P2_1mn$. The remaining atoms are located by difference syntheses. A full-matrix least-squares refinement including a weighting scheme ($w = 1/[\sigma^2(F) + 0.01570F^2]$) converges to $R = 0.062$ and $R_w = 0.060$ with anisotropic thermal parameters except for Cl and O of ClO_4 and C of ethanol and methyls of NIPA. H atoms were not located. Atomic scattering factors and anomalous dispersion for U were taken from ref 10. Final positional and thermal parameters are given in Table III. A list of calculated and observed factors is available.[12]

Method of Theoretical Calculation and Procedure

The energy of the NIPA molecule has been calculated by the semiempirical CNDO/2 method[13] using the program GEOMO.[14] A spd basis for the phosphorus atom orbitals has been chosen.[15,16] Methyl groups were substituted by hydrogen atoms for simplification and the geometrical parameters were obtained from crystallographic data. Only the angle ϕ, which describes the

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Table II. Positional and Thermal Parameters ($\times 10^4$) for Non-Hydrogen Atoms of NIPA

atoms	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq}, Å^2
P(1)	7431 (1)	2811 (1)	3243 (0)	458 (4)	472 (4)	333 (3)	−63 (3)	97 (3)	−30 (3)	3.31 (2)
P(2)	7154 (1)	2209 (1)	1593 (0)	330 (3)	528 (4)	340 (3)	−77 (3)	79 (2)	27 (3)	3.14 (2)
O(1)	5713 (3)	2908 (2)	3616 (1)	628 (12)	870 (15)	555 (11)	−40 (11)	285 (9)	11 (11)	5.22 (6)
O(2)	9119 (3)	1753 (2)	1792 (1)	349 (9)	771 (14)	585 (11)	−88 (10)	90 (8)	97 (9)	4.49 (5)
N(1)	6695 (3)	2943 (2)	2289 (1)	532 (12)	456 (12)	344 (9)	−72 (9)	51 (8)	110 (10)	3.55 (5)
N(2)	9079 (3)	3687 (2)	3481 (1)	618 (14)	511 (14)	473 (12)	−113 (10)	56 (11)	−122 (11)	4.28 (6)
N(3)	8551 (3)	1752 (2)	3442 (1)	600 (13)	474 (13)	456 (11)	6 (10)	64 (10)	−30 (11)	4.07 (6)
N(4)	5311 (3)	1425 (2)	1433 (1)	398 (11)	711 (16)	624 (13)	−289 (12)	139 (10)	−64 (11)	4.52 (6)
N(5)	6941 (4)	2863 (2)	809 (1)	699 (15)	823 (18)	388 (11)	54 (12)	140 (11)	79 (14)	5.00 (7)
C(1)	5372 (8)	3805 (3)	2071 (2)	1089 (30)	694 (25)	526 (18)	−76 (18)	42 (21)	443 (23)	6.2 (1)
C(2)	10438 (7)	4036 (4)	3010 (3)	829 (28)	832 (31)	873 (28)	−103 (24)	220 (22)	−380 (25)	6.6 (1)
C(3)	9569 (8)	3997 (4)	4274 (2)	952 (32)	924 (36)	607 (22)	−313 (22)	−80 (22)	−101 (29)	6.8 (1)
C(4)	10671 (5)	1587 (4)	3504 (2)	632 (21)	722 (26)	744 (23)	41 (22)	−17 (17)	146 (20)	5.7 (1)
C(5)	7368 (7)	863 (3)	3421 (3)	1050 (33)	504 (21)	714 (24)	7 (18)	172 (23)	−157 (21)	6.0 (1)
C(6)	5344 (7)	655 (4)	862 (3)	659 (23)	904 (31)	903 (29)	−484 (25)	96 (22)	−26 (22)	6.6 (1)
C(7)	3512 (5)	1450 (4)	1721 (3)	452 (17)	967 (31)	826 (25)	−168 (24)	208 (17)	−158 (19)	5.8 (1)
C(8)	8673 (9)	3388 (4)	649 (3)	1237 (40)	1035 (40)	750 (27)	55 (27)	419 (28)	−295 (32)	7.7 (2)
C(9)	5074 (8)	3078 (4)	281 (2)	1047 (34)	1273 (42)	418 (16)	85 (20)	22 (19)	440 (30)	7.3 (2)

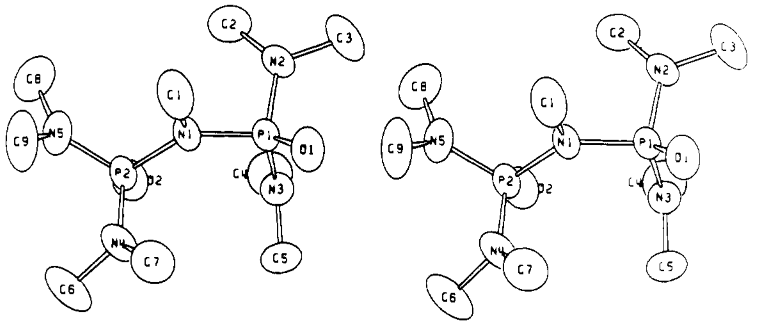

Figure 1. Stereoscopic ORTEP view of NIPA.

rotation of a P(O)(NH$_2$)$_2$ group with respect to the other part of the molecule, was varied. Program GEOMO allows to simulate the liquid surroundings of a molecule on the base of a cavity model;[17] in the case of NIPA, we used a spherical cavity, the volume of which was equal to the molecular volume of NIPA: 408 Å^3. The dielectric constant of the solvent was taken equal to 25, an approximate value corresponding to the solvent used in the NMR studies.

Coupling-constant calculations were carried out with the CNDO/2 method;[16] the Fermi contact term represents the principal part of the mechanism of spin–spin scalar coupling between directly bound atoms.[18] The ρ density of the 3s orbital of phosphorus (5.625 au) was taken from ref 19, and nuclear magnetic parameters from ref 20.

Results and Discussion

Crystal Structure Analysis. The molecular geometry of free NIPA, including the atomic numbering scheme, is illustrated by the stereoscopic ORTEP view[21] on Figure 1. Table IV gives bond lengths and angles. P(1), P(2), N(1), and C(1) are coplanar: they are located respectively at −0.007 (1), −0.008 (1), 0.023 (2), and −0.008 (5) Å from the least-squares plane. The dihedral angle between the P(1)–P(2)–O(1) and P(1)–P(2)–O(2) planes is 149.3 (1)°. Thus the NIPA molecule in the solid state is in a trans conformation. All the C$_2$NP groups are nearly planar as aleady noticed by Joesten et al.[22] for a similar molecule, octamethylpyrophosphoramide, and by Lapidaire et al.[23] for a tridentate ligand, dodecamethyldiimidotriphosphoramide (TRIPA). This implies that all nitrogen atoms of the free NIPA molecule show trigonal hybridization.

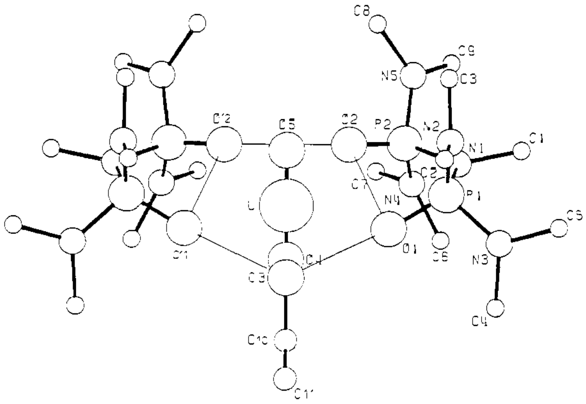

Figure 2. Projection of complex B on (001).

Figure 2 illustrates the geometry of complex B by a projection on (001). Table V gives distances and angles around the U atom. The U–O(4) and U–O(5) distances of 1.75 (1) and 1.73 (1) Å are those commonly encountered for the UO$_2^{2+}$ ion.[10] The UO$_2^{2+}$ unit is linear and perpendicular to the pentagon O(1), O(2), O′(1), O′(2), O(3), formed by the oxygen atoms of the two bidentate NIPA molecules and the ethanol entity. Nevertheless, the pentagon is not exactly planar: O(3), the oxygen of ethanol, is slightly out of the O(1), O(2), O′(1), O′(2) plane (by 0.26 (1) Å).

To our knowledge no other structures of uranyl complexes containing β-biphosphorylated ligands have been described in the literature. However, monophosphorylated compounds such as HMPA (hexamethylphosphorotriamide), TBPO (tributylphosphine oxide), or TMP (trimethylphosphate) form complexes

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Table III. Positional and Thermal Parameters (×10^4) of Complex B

atoms	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq}, Å^2
U	0	0	2036 (0)	460 (3)	305 (2)	446 (3)	0	4 (5)	0	3.19 (1)
O(1)	−613 (11)	1467 (7)	1806 (7)	468 (17)	399 (17)	869 (17)	53 (17)	−189 (17)	54 (17)	4.57 (8)
O(2)	1656 (12)	905 (7)	2752 (6)	652 (17)	468 (17)	618 (17)	−88 (17)	−201 (17)	−14 (17)	4.57 (8)
O(3)	−1918 (14)	0	1066 (9)	669 (18)	524 (17)	764 (18)	0	−180 (18)	0	5.15 (8)
O(4)	−1470 (14)	0	2711 (9)	614 (18)	529 (17)	669 (17)	0	309 (17)	0	4.77 (8)
O(5)	1473 (13)	0	1375 (8)	304 (17)	910 (18)	673 (18)	0	111 (17)	0	4.97 (8)
P(1)	308 (5)	2295 (2)	1755 (2)	531 (15)	346 (10)	679 (13)	45 (11)	−88 (13)	−15 (12)	4.09 (6)
P(2)	1703 (6)	1721 (3)	3140 (2)	664 (15)	488 (13)	510 (13)	−80 (12)	−50 (13)	−102 (13)	4.38 (6)
N(1)	1149 (14)	2488 (7)	2555 (7)	882 (18)	340 (17)	757 (18)	−11 (17)	−132 (17)	−111 (17)	5.21 (8)
N(2)	1688 (14)	2330 (10)	1162 (8)	720 (18)	792 (18)	791 (18)	28 (18)	−5 (18)	−207 (18)	6.06 (8)
N(3)	−984 (13)	3058 (7)	1526 (9)	756 (18)	384 (17)	1025 (18)	223 (17)	−67 (18)	37 (17)	5.70 (8)
N(4)	611 (15)	1847 (9)	3842 (9)	1482 (18)	596 (17)	910 (18)	−4 (17)	−18 (18)	418 (18)	7.87 (8)
N(5)	3529 (15)	1843 (9)	3434 (8)	1055 (18)	660 (17)	847 (18)	−148 (17)	−283 (18)	−93 (18)	6.74 (8)
C(1)	1513 (16)	3426 (12)	2765 (11)	888 (17)						7.0 (1)
C(2)	1233 (16)	2231 (14)	415 (12)	1133 (18)						8.9 (1)
C(3)	3360 (16)	2310 (13)	1296 (11)	968 (17)						7.6 (1)
C(4)	−2706 (16)	3019 (14)	1795 (12)	1071 (17)						8.5 (1)
C(5)	−554 (16)	3903 (13)	1205 (11)	1025 (17)						8.1 (1)
C(6)	−947 (16)	2279 (13)	3857 (11)	1039 (17)						8.2 (1)
C(7)	959 (17)	1323 (15)	4519 (13)	1479 (18)						11.7 (1)
C(8)	4888 (17)	1315 (14)	3116 (11)	1138 (7)						9.0 (1)
C(9)	3878 (17)	2427 (15)	4049 (13)	1304 (18)						10.3 (1)
Cl(1)	4238 (8)	5000	870 (4)	714 (12)						5.6 (1)
O(6)	3767 (17)	4313 (15)	427 (13)	2478 (18)						19.6 (1)
O(7)	3551 (18)	5000	1432 (16)	2478 (18)						19.6 (1)
O(8)	5633 (17)	5000	1098 (16)	2478 (18)						19.6 (1)
Cl(2)	1002 (12)	5000	4745 (6)	1142 (15)						9.0 (1)
O(9)	2065 (17)	5734 (15)	4667 (14)	2536 (18)						20.0 (1)
O(10)	620 (17)	5000	3964 (16)	2536 (18)						20.0 (1)
O(11)	−332 (18)	5000	5067 (16)	2536 (18)						20.0 (1)
C(10)	6443 (17)	322 (15)	1037 (14)	787 (18)						6.2 (1)
C(11)	5452 (17)	0	744 (15)	1489 (18)						11.8 (1)

Table IV. Bond Lengths and Angles of NIPA

atoms	distances, Å	atoms	distances, Å
P(1)–O(1)	1.472 (2)	N(2)–C(2)	1.455 (6)
P(1)–N(1)	1.683 (2)	N(2)–C(3)	1.449 (5)
P(1)–N(2)	1.639 (2)	N(3)–C(4)	1.454 (5)
P(1)–N(3)	1.639 (2)	N(3)–C(5)	1.453 (5)
P(2)–O(2)	1.463 (2)	N(4)–C(6)	1.465 (6)
P(2)–N(1)	1.671 (2)	N(4)–C(7)	1.431 (5)
P(2)–N(4)	1.635 (2)	N(5)–C(8)	1.465 (7)
P(2)–N(5)	1.637 (2)	N(5)–C(9)	1.458 (5)
N(1)–C(1)	1.486 (5)		
atoms	**angles, deg**	**atoms**	**angles, deg**
O(1)–P(1)–N(2)	113.1 (1)	C(1)–N(1)–P(2)	118.4 (2)
O(1)–P(1)–N(3)	111.4 (1)	P(1)–N(2)–C(2)	125.3 (2)
O(1)–P(1)–N(1)	110.0 (1)	P(1)–N(2)–C(3)	118.5 (3)
N(1)–P(1)–N(2)	103.6 (1)	C(2)–N(2)–C(3)	114.7 (3)
N(1)–P(1)–N(3)	110.2 (1)	P(1)–N(3)–C(4)	124.8 (2)
N(2)–P(1)–N(3)	108.3 (1)	P(1)–N(3)–C(5)	119.4 (2)
O(2)–P(2)–N(4)	114.1 (1)	C(4)–N(3)–C(5)	114.8 (3)
O(2)–P(2)–N(5)	110.9 (1)	P(2)–N(4)–C(6)	117.9 (2)
O(2)–P(2)–N(1)	112.1 (1)	P(2)–N(4)–C(7)	128.1 (3)
N(1)–P(2)–N(4)	105.3 (1)	C(6)–N(4)–C(7)	113.6 (3)
N(1)–P(2)–N(5)	108.0 (1)	P(2)–N(5)–C(8)	119.7 (2)
N(4)–P(2)–N(5)	105.9 (1)	P(2)–N(5)–C(9)	125.1 (3)
P(1)–N(1)–P(2)	128.5 (1)	C(8)–N(5)–C(9)	114.7 (3)
C(1)–N(1)–P(1)	113.0 (2)		

Table V. Distances and Angles around U in Complex B[a]

atoms	distances, Å	atoms	angles, deg
U–O(1)	2.36 (1)	O(4)–U–O(1)	88.4 (3)
U–O(2)	2.37 (1)	O(4)–U–O(2)	91.3 (4)
U–O(3)	2.40 (1)	O(4)–U–O(3)	93.0 (6)
U–O(4)	1.75 (1)	O(5)–U–O(1)	91.8 (3)
U–O(5)	1.73 (1)	O(5)–U–O(2)	88.2 (4)
O(1)–O(2)	2.72 (1)	O(5)–U–O(3)	87.7 (5)
O(1)–O(3)	2.86 (1)	O(4)–U–O(5)	179.3 (6)
O(2)–O′(2)	2.80 (2)	U–O(1)–P(1)	135.9 (6)
		U–O(2)–P(2)	143.6 (6)

[a] Equivalent positions: x, y, z; (′) $x, -y, z$; (″) $^1/_2 + x, {}^1/_2 + y, -z$; (‴) $^1/_2 + x, {}^1/_2 - y, -z$.

in which the coordination number of UO_2^{2+} varies between 4 and 6.

A comparison of the HMPA complexes with complex B is of special interest since NIPA may be considered as a dimer of HMPA.

In the complexes $[UO_2(HMPA)_2Cl_2]$,[24,25] $[UO_2(HMPA)_4](I_3)_2$,[26] $[UO_2(HMPA)_4](ClO_4)_2$,[27] and B the U–OP bond length increases in the order 2.272 (9) < 2.290 (8) ≃ 2.28 (5) <2.365 (10) Å.

The reason for this is most probably the enhanced crowding of the ligand molecules around the UO_2^{2+} ion. The fact that the highest value is observed for complex B is due to a coordination number of 5 in this case whereas the other moieties are four-coordinate.

This agrees with the fact that in the six-coordinate complex $[UO_2(TMP)_2(NO_3)_2]$[28] containing only two bulky TMP molecules but also two smaller bidentate nitrate groups the U–OP distance is about equal to that found for complex B (2.35 (1) Å).

Table VI indicates bond lengths and angles of the bound NIPA ligand. P(1), P(2), N(1), and C(1) are coplanar at 0.005 (4), 0.005 (5), −0.016 (12), and 0.005 (15) Å from the least-squares plane. The P(1)–P(2)–O(1) and P(1)–P(2)–O(2) planes form an angle of 40.5 (6)°. The coordinated ligand NIPA presents therefore a cis conformation. Like in free NIPA, all nitrogen atoms are in sp^2 hybridization.

The most striking difference between the geometries of NIPA free and bound in complex B is the change from a trans to a cis

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Table VI. Bond Lengths and Angles of Bound NIPA in Complex B

atoms	distance, Å	atoms	distance, Å
P(1)-O(1)	1.50 (1)	N(2)-C(2)	1.43 (3)
P(1)-N(1)	1.66 (1)	N(2)-C(3)	1.43 (2)
P(1)-N(2)	1.59 (1)	N(3)-C(4)	1.53 (2)
P(1)-N(3)	1.66 (1)	N(3)-C(5)	1.48 (2)
P(2)-O(2)	1.45 (1)	N(4)-C(6)	1.47 (2)
P(2)-N(1)	1.67 (1)	N(4)-C(7)	1.51 (3)
P(2)-N(4)	1.59 (2)	N(5)-C(8)	1.52 (2)
P(2)-N(5)	1.64 (1)	N(5)-C(9)	1.48 (3)
N(1)-C(1)	1.53 (2)		
atoms	**angles, deg**	**atoms**	**angles, deg**
O(1)-P(1)-N(2)	116.6 (7)	C(1)-N(1)-P(2)	117 (1)
O(1)-P(1)-N(3)	106.6 (6)	P(1)-N(2)-C(2)	117 (1)
O(1)-P(1)-N(1)	108.5 (7)	P(1)-N(2)-C(3)	127 (1)
N(1)-P(1)-N(2)	106.8 (7)	C(2)-N(2)-C(3)	115 (1)
N(1)-P(1)-N(3)	112.1 (7)	P(1)-N(3)-C(4)	121 (1)
N(2)-P(1)-N(3)	106.2 (7)	P(1)-N(3)-C(5)	125 (1)
O(2)-P(2)-N(4)	119.2 (7)	C(4)-N(3)-C(5)	113 (1)
O(2)-P(2)-N(5)	106.7 (7)	P(2)-N(4)-C(6)	126 (1)
O(2)-P(2)-N(1)	107.1 (7)	P(2)-N(4)-C(7)	119 (1)
N(1)-P(2)-N(4)	105.9 (7)	C(6)-N(4)-C(7)	114 (1)
N(1)-P(2)-N(5)	113.1 (7)	P(2)-N(5)-C(8)	121 (1)
N(4)-P(2)-N(5)	105.0 (8)	P(2)-N(5)-C(9)	121 (1)
P(1)-N(1)-P(2)	124.3 (7)	C(8)-N(5)-C(9)	118 (1)
C(1)-N(1)-P(1)	118 (1)		

Table VII. Mean Values of P-O and P-N Bond Lengths (Å) in NIPA and TRIPA

	NIPA		TRIPA	
bonds	free	complex B	free[23]	in complexes[a]
P-O	1.467 (2)	1.475 (10)	1.470 (2)	1.493 (2)
P-N (bridge)	1.677 (2)	1.665 (10)	1.680 (1)	1.674 (5)
P-N (terminal)	1.637 (1)	1.620 (6)	1.631 (1)	1.627 (4)

[a] Mean values for $Er(TRIPA)_2(NO_3)_3$(acetone) and $[Ca(TRIPA)(NO_3)_2(H_2O)]$.[29]

conformation of the P=O groups. The same phenomenon is observed for the TRIPA molecule for which the trans-trans conformation of the P=O bonds in the "free" state[23] (actually with an hydrogen bonded water molecule) becomes cis-cis when coordinated to Ca^{2+} or Er^{3+} cations.[29] Table VII summarizes the mean values of the P=O and P—N bond lengths in NIPA and TRIPA.[23] On one hand all P-N bonds are shorter than the accepted values for a P-N single bond[10] (1.78 Å), which can be ascribed to interactions of the lone pair on the nitrogen atoms and empty d orbitals on the phosphorus atoms; there are two types of P-N bonds: the terminal P-N distances are shorter than the bridging P-N bonds. On the other hand the bond lengths vary between the free molecule and the ligand: P=O bonds increase when P—N bonds (bridge and terminal) decrease.

It may be noted that the compound similar to NIPA in which S atoms replace the oxygens presents also in the free molecule a trans conformation for the P=S bonds lying in the P—N—P plane.[30]

Theoretical Calculations and NMR Studies. Theoretical calculations show that the trans conformation is energetically more stable than the cis arrangement for an isolated NIPA molecule (Figure 3). The activation energy for the rotation of a $P(O)(NH_2)_2$ group with respect to the other part of the molecule approaches 15 kJ mol^{-1}. However, on simulating the environment of the NIPA molecule as if it were surrounded by a solvent with a dielectric constant of 25, the "cis" form is the stable conformation. This suggests that intermolecular (solvent-solute) dipole-dipole interactions predominate over the intramolecular repulsion forces between the two P=O dipoles.

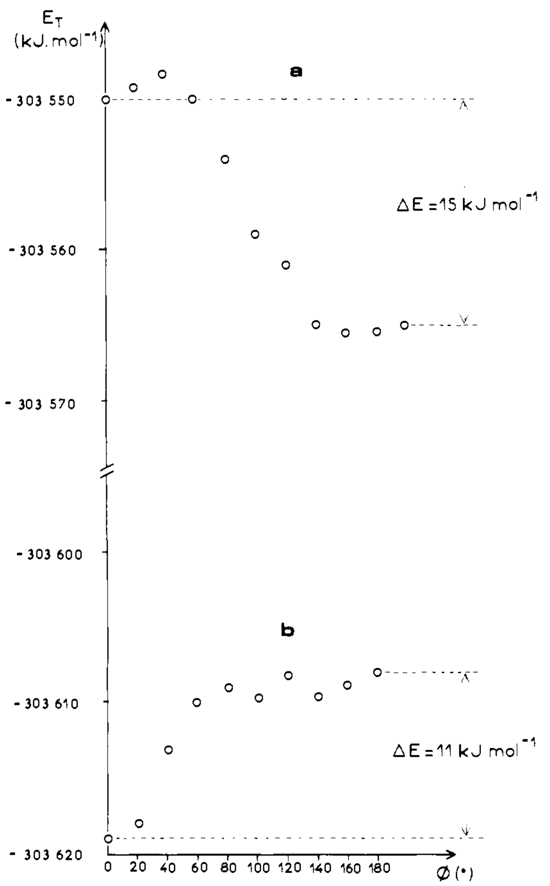

Figure 3. Calculated total energy of NIPA isolated (a) and surrounded by a polar solvent (b) as a function of the dihedral angle between the two P=O groups.

Table VIII. Theoretical and Experimental $^2J_{PP}$ and $^1J_{PN}$ Values (Hz) for NIPA Isolated and in Solution

conformation	coupling const	theor isolated	theor soln	exptl (abs values)
cis	$^2J_{PP}$	−11	−11	15.6
cis	$^1J_{PN}$	−20	−24	33.4
trans	$^2J_{PP}$	−15	−13	22.0
trans	$^1J_{PN}$	−23	−28	not determined

At the sight of these results it was interesting to try to ascertain the NIPA conformation in solution experimentally. This was done by measuring the value of the coupling constant $^2J_{P-P}$ between the two phosphorus atoms in the "free" NIPA. In fact we had observed earlier[4] that the coupling constant of the bidentate ligand ($|J|$ = 15.6 Hz) was different from that of the monodentate NIPA ($|J|$ = 22.0 Hz). In the first case the conformation of the molecule is cis. In the other case, the value of J indicates a change of geometry (probably to a trans conformation). Assuming that the J value is not affected by coordination, its measurement allows the determination of the geometry of NIPA in solution. The coupling constant $^2J_{P-P}$ is not directly observed on $^{31}P\{^1H\}$ NMR spectra since the two phosphorus nuclei are equivalent. Nevertheless it is possible to determine its value if the ^{15}N satellites in the ^{31}P spectrum can be detected. (Attempts to observe the ^{13}C satellites failed because of the very small values of $^{31}P-^{13}C$ couplings[31]). In the molecules with a ^{15}N nucleus (of natural abundance in our experiments) the symmetry is removed and an ABX system[32] is formed, where A is the ^{31}P nucleus directly bound

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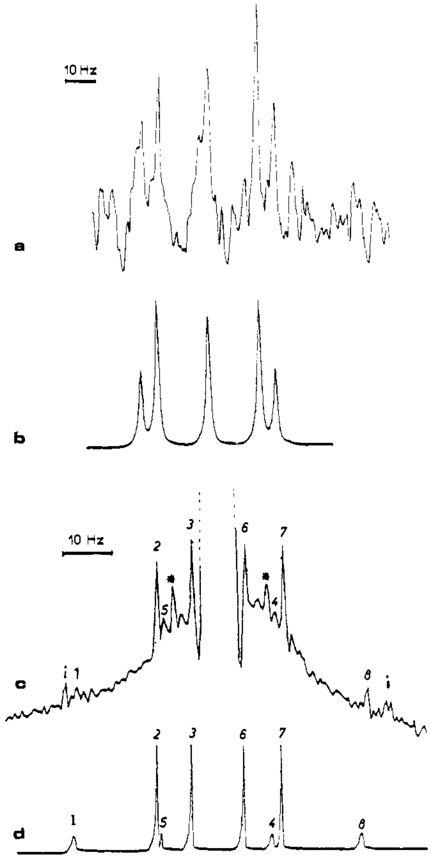

Figure 4. Experimental $^{15}N\{^1H\}$ (a) and $^{31}P\{^1H\}$ (c) NMR spectra of NIPA in C_2N solution; (b) and (d), calculated subspectra for the ABX case formed by the $^{15}N(X)$, $^{31}P(A)$, and $^{31}P(B)$ nuclei (J_{AB} = 15.6, J_{AX} = 33.4, J_{BX} = 0.75 Hz, and $\nu_A - \nu_B$ = 0.3 Hz). The lines marked by asterisks are probably due to coupling with the central N atom. Lines i are signals of an impurity.

to ^{15}N and B is the phosphorus two bonds removed. From ^{15}N and ^{31}P NMR spectra $|^2J_{P-P}|$ and $|^1J_{P-N}|$ values of 15.6 and 33.4 Hz, respectively, are obtained (Figure 4). The former value is exactly equal to that observed for coordinated bidentate NIPA; we conclude that "free" NIPA, in a polar medium, is in the cis conformation. For the TRIPA ligand in pure dichloromethane, a less polar solvent, Scholer[33] proposes a trans–trans conformation. These results stress the importance of the polarity of the medium, solvents of high dipolar moment favoring the more polar (cis) form of the solute. The $|^1J_{P-N}|$ value is comparable to that obtained in the case of hexamethylphosphoramide[18] ($|J_{P-N}|$ = 26.9 Hz).

The results of theoretical calculations of the coupling constants J_{P-P} and J_{P-N} are reported in Table VIII together with the experimental constants. The $|J_{P-N}|$ values obtained when a solvent is simulated are 25% higher than those calculated for an isolated molecule. On the contrary, $|J_{P-P}|$ is slightly lower when NIPA is surrounded by solvent molecules. Among the values calculated for a liquid medium, $|J_{P-P}|$ and $|J_{P-N}|$ are more important for the trans than for the cis conformation, as it has been shown experimentally. The computed J_{P-N} and J_{P-P} values agree well with the experimental ones: 24 compared to 33.4 and 11 compared to 15.6 Hz. (In our NMR experiences we did not determine the sign of the coupling constants).

Conclusions

The combined results from X-ray diffraction studies, NMR spectroscopy, and theoretical calculations show that a neutral, β-biphosphorylated ligand like NIPA can assume different geometries, depending on its environment. In the presence of ions or sufficiently polar solvent molecules the cis form is largely favored, whereas a trans conformation is found for the pure ligand reflecting an energy minimum of the isolated molecule when the P=O groups are arranged in opposite directions. Moreover, the proof by X-ray analysis of a trans conformation for solid NIPA confirms our previous hypothesis concerning the complex $UO_2(NIPA)_3^{2+}$ for which we postulated, for steric reasons, the existence of a monodentate NIPA molecule in trans conformation.

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Supplementary Material Available: Positional and thermal parameters for the hydrogen atoms of NIPA as well as observed and calculated structure factors for NIPA and complex B (29 pages). Ordering information is given on any current masthead page.

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