A REVISION OF THE GUTMANN DONOR NUMBERS OF A SERIES OF PHOSPHORAMIDES INCLUDING TEPA

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The donor numbers (*DN*) of a series of 20 phosphoramides with general structure $(R_2N)(X_2N)(Y_2N)P=O$ (with R,X and Y alkyl radicals, nitrogen-heterocycles or hydrogen atoms) were revised on the basis of a series of rather simple considerations. It is shown that all the phosphoramides considered even after the revision are characterized by high *DN*. In a scale of 163 different type of solvent molecules, the phosphoramides are all collocated with their *DN* above 35 kcal mol^{-1} till 50 kcal mol^{-1}. The extremely high *DN* value reported previously for (tris(1-aziridinyl)phosphine oxide (TEPA), is now revised to 50 kcal mol^{-1}. The highest *DN* values in the phosphoramides considered in this investigation were those of TEPA, $(NHEt)_3P=O$ and $(pyrrolidino)_3P=O$.

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Introduction

Different methodologies and scales are available to measure the polarity of solvents, their ability to act as electron pair donors, electron pair acceptors and their interaction with solutes and electrolytes. One of the most comprehensive reviews on this topic can be found in the book of Reichardt and references reported therein.[1]

One of the earlier way to measure the Lewis base behaviour of a solvent was proposed by Gutmann and led to the development of the Gutmann's Donor Number (*DN*) or donicity of a solvent.[2-6] The measurement of the *DN* involves the use of a relatively strong electron pair acceptor (Lewis acid), antimony pentachloride ($SbCl_5$), and its formation of a 1:1 adduct with the solvent under study in an inert medium (1,2-dichloroethane). The enthalpy of this exothermal reaction (1) is corrected with the mixing enthalpy of the solvent under study S: dissolved in an inert medium 1,2-dichloroethane (DCE).

$$S: + SbCl_5 \rightarrow [S \rightarrow SbCl_5] + \Delta H_{adduct} \quad (1)$$

$$S: + DCE \rightarrow S(DCE) + \Delta H_{mix} \quad (2)$$

so that

$$DN = - \Delta H_{donor} = \Delta H_{adduct} - \Delta H_{mix} \quad (3)$$

The donor number is expressed in kcal mol^{-1} although it can be used in a normalized dimensionless scale the DN^N which is obtained by dividing the following relationship.[1]

$$DN^N = DN/38.8 \quad (4)$$

Since the *DN* value is expressed in kcal mol^{-1} and 38.8 kcal mol^{-1} is the *DN* value of hexamethyl phosphoric acid triamide (HMPT), a solvent with high donicity, then the DN^N is a dimensionless number.

The stronger is the bond in the 1:1 adduct formed between $SbCl_5$ and the solvent, the higher is the reaction enthalpy and hence higher is the donor number.

The *DN* scale is very useful for chemists and although many other scales have been developed, it remains an important reference as shown by very recent publications.[7-9] A similar solvent scale known as "Gal and Maria scale" was developed using another stronger Lewis acid: boron trifluoride, measuring again the enthalpy of reaction in the formation of the 1:1 adduct $-\Delta H_{D\text{-}BF3}$ and expressed in kJ mol^{-1}.[1,7] Of course, there is a pretty nice correlation between the *DN* scale and the Gal and Maria Scale of values.[1,7]

Our interest is currently focused on the *DN* properties of the phosphoramides and the sulphur analogous thiophosphoramides, whose general structures are as follows.

$$(R_2N)(X_2N)(Y_2N)P=O$$

and

$$(R_2N)(X_2N)(Y_2N)P=S$$

where R, X, Y can be any kind of alkyl radical, nitrogen heterocyclic or hydrogen atom. These molecules have a series of interesting and sometimes unique applications and properties. The most known phosphoramide is hexamethyl phosphoric acid triamide, $[(CH_3)_3N]_3P=O$ (abbreviated HMPT and sometimes also HMPA) which has found a wide application as solvent in organic chemistry some time ago and whose use is now limited after the discovery of its carcinogenetic nature in animals.[10,11]

Other well known phosphoramides are METEPA [tris(2-methylaziridinyl)phosphine oxide] and TEPA which are used as crosslinking agents in dyeing, crease proofing and flame proofing of textiles, as crosslinkers and stabilizers in polymer chemistry and as an insect chemosterilants.[12] METEPA is also a well known antineoplastic agent which, together with its thio analogue THIOTEPA, is adopted in cancer chemiotherapy.[12] Phosphoramides are also interesting because their ability to act as inhibitors of enzymatic reactions.[13,14] In all the above applications the unique donicity properties of phosphoramides are put in place.

The *DN* number of a series of phosphoramides, including TEPA were measured some time ago[15] and reported recently in a review without any substantial critical discussion and revision.[7] The purpose of the present work is to discuss and revise the *DN* values of phosphoramides measured in ref. [15]

Results and Discussion

Among the solvents whose *DN* number has been measured according to the Gutmann method (eqn. 1-3), a series of phosphoramides are reported as compounds with high and very high *DN* values.[7,15] Particularly impressive is the fact that the compound with the strongest donicity in absolute appears to be TEPA with a *DN*= 91.5 kcal mol^{-1}.[7,15]

The widely accepted and used *DN* value of HMPT is 38.8 kcal mol^{-1}, [1,16] while in a paper dedicated to phosphoramides by Bollinger et al., the *DN* value of HMPT was reported as 50.3 kcal mol^{-1}.[15] As commented by Reichardt,[1] this important difference in the *DN* value for a molecule selected for the *DN* scale normalization shows that "serious problems arise in measuring [calorimetrically] the Lewis basicity of this electron pair donor solvent towards $SbCl_5$". As a consequence of these differences in the measured *DN* values of HMPT, usually the phosphoramides *DN* values are omitted in general reviews of solvents[1] or are reported without any further comment.[7]

To arrive at useful *DN* values of phosphoramides and to make a suitable comparison with the *DN* values of other solvents, we propose a simple and operative approach. Since Bollinger et al[15] have reported the *DN* values of the phosphoramides taking that of HMPT as 50.3 kcal mol^{-1} against the commonly accepted value of 38.8 kcal mol^{-1}, we propose here to normalize the *DN* values of all the phosphoramides by a correction factor, A = 38.8/50.3 = 0.7714.

In this way, not only the HMPT value is brought at 38.8 kcal mol^{-1}, but also all the other phosphoramides values are corrected with the same factor and can be harmonized with the *DN* values of other solvents. This correction does not necessarily implies that the *DN* values of phosphoramides in the paper of Bollinger et al. are affected by a systematic error, but it is reasonable to apply to all of them the correction factor which is *de facto* applied to the key phosphoramide, HMPT.

Furthermore, the *DN* value of $(Me_2N)_2$(pyrrolidino)P=O (MPPA) was measured as 51.1 kcal mol^{-1} by Bollinger et al,[15] while other authors have found it be 38.0 kcal mol^{-1}.[16] Once again a correction factor B of 0.7436 should be applied to bring the *DN* value from 51.1 to 38.0 kcal mol^{-1}. It is curious to note here how close each other are the correction factors A and B. Another example of this situation is offered by the case of (pyrrolidino)$_3$P=O (TPPT or TPPA) whose *DN* value was found to be 54.8 kcal mol^{-1} by Bollinger et al,[15] while it was found later as 47.2 kcal mol^{-1} by other authors,[16] requiring a correction factor C of 0.8613 to go from the higher *DN* value to the lower value.

In Table 1 we applied the three correction factors A, B and C as determined above to the *DN* values of phosphoramides measured by Bollinger et al.[15] With this operation, the *DN* of phosphoramides appear more homogeneous each other and may be more comparable to the *DN* value of other solvents.

A key consideration regards the basicity of each amine attached to the P=O group. The pK_b values of some of the bases are given below.[17]

Aziridine = 5.96, azetidine = 2.71, pyrrolidine = 2.73, piperidine = 2.80, $(CH_3)NH_2$ = 3.37, $(CH_3)_2NH$ = 3.22, $(CH_3)_3N$ = 4.20, $EtNH_2$ = 3.27, Et_2NH = 2.89, Et_3N = 3.36

It should be noted here that stronger bases have low pK_b and are able bind strongly a proton (H^+) than a weaker base which instead has a high pK_b value. In other words, stronger bases are excellent lone pairs donors binding the H^+ ion. Once the amine is attached to the P=O group in the phosphoramide molecule, strong bases act as electron attractors and reduce the lone pair charge on the P=O oxygen, thus reducing the *DN*. On the other hand weaker bases would attract the electron less, causing less decrease in the charge concentration of the oxygen lone pair in the P=O group, thus enhancing the *DN*. From the pK_b data presented here, all the amine groups including the heterocycles, with the exception of aziridine, are strong bases. Consequently, we should not expect any large difference in the *DN* value by passing from azetidine to pyrrolidine or to piperidine. Looking at the *DN* values in Table 1, especially those multiplied by the correction factor A (fourth column from the right), one can see that the *DN* values are all similar, as expected and range between 40 and 48 kcal mol^{-1}. Furthermore, partial substitution or complete substitution of heterocyclic amines as phosphoramide substitutents with aliphatic amines has a minor impact since all values remain around 40 kcal mol^{-1} in line with the *DN* value of HMPT of 38.8 kcal mol^{-1}.

Table 1 also shows that the introduction of a pyrrolidine moiety in phosphoramide as replacement of a dimethylamino unit causes very limited changes in the *DN* value.[16]

$(NMe_2)_3P=O \rightarrow (NMe_2)_2(pyrrolidino)P=O \rightarrow$ (5)

[*DN*= 38.8] [*DN*= 38.0]

$(NMe_2)(pyrrolidino)_2P=O \rightarrow (pyrrolidino)_3P=O$ (6)

[*DN*= 45.4] [*DN*= 47.2]

The trend is confirmed also by the data of Bollinger et al[15] not only in the case of the pyrrolidine but also in the case of the other nitrogen heterocycles considered, i.e. azetidine and piperidine.

Table 1. *DN* values of phosphoramides with and without using correction factors

Phosphoramide	**Original *DN* Values ref. 15 *DN***	***DN* values from ref. 16 *DN***	**Correction factor *A* = 0.7714 *DN* corr A**	**Correction factor *B* = 0.7436 *DN* corr B**	**Correction factor *C* = 0.8613 *DN* corr C**	**Recommen-ded values**
$(EtO)_3P=O$	24.0		24.0			24.0
$(NMe_2)(EtO)_2P=O$	29.5		29.5			29.5
$(NMe_2)_2(EtO)P=O$	47.2		36.4	35.1	40.7	36.4
$(NMe_2)_3P=O$ (HMPA or HMPT)	50.3	38.8	38.8	37.4	43.3	38.8
$(NEt_2)_3P=O$	47.4		36.6	35.2	40.8	36.6
$(NMe)_2(MeN\text{-}CH_2\text{-}CH_2\text{-}NMe)P=O$	54.6		42.1	40.6	47.0	42.1
$(NMe2)_2(NEt_2)2P=O$	49.0		37.8	36.4	42.2	37.8
$(NMe_2)_2(NHEt)P=O$	53.4		41.2	39.7	46.0	41.2
$(NMe_2)(NHEt)_2P=O$	52.6		40.6	39.1	45.3	40.6
$(NHEt)_3P=O$	61.3		47.3	45.6	52.8	47.3
$(piperidino)_3P=O$	53.0		40.9	39.4	45.6	40.9
$(NEt_2)(pyrrolidino)_2P=O$	55.2		42.6	41.0	47.5	42.6
$(NEt_2)_2(pyrrolidino)P=O$	52.1		40.2	38.7	44.9	40.2
$(NMe_2)_2(pyrrolidino)P=O$ (MPPA)	51.1	38.0	39.4	38.0	44.0	38.0
$(NMe_2)(pyrrolidino)_2P=O$ (DPPA)	49.4	45.4	38.1	36.7	42.5	45.4
$(pyrrolidino)_3P=O$ (TPPA or TPPT)	54.8	47.2	42.3	40.7	47.2	47.2
$(NMe_2)_2(azetidino)P=O$	53.3		41.1	39.6	45.9	41.1
$(NMe_2)(azetidino)_2P=O$	54.8		42.3	40.7	47.2	42.3
$(azetidino)_3P=O$	55.7		43.0	41.4	48.0	43.0
$(NMe_2)_2(aziridino)P=O$	63.0		48.6	46.8	54.3	48.6
$(NMe_2)(aziridino)_2P=O$	63.6		49.1	47.3	54.8	49.1
$(aziridino)_3P=O$ (TEPA)	91.5		70.6	68.0	78.8	50.0

The unique exception to the above trend is represented by the substitution by aziridine in phosphoramides:

$(NMe_2)_3P=O \rightarrow (NMe_2)_2(aziridino)P=O \rightarrow$
[*DN*= 38.8] [*DN*= 48.6]

$(NMe_2)(aziridino)_2P=O \rightarrow (aziridino)_3P=O$ (7)
[*DN*= 49.1] [*DN*= 70.6 ?]

The enhancement of the *DN* is expected since aziridine is the weaker base of all amines considered here and is much weaker also than dimethylamine. Thus, the passage from 38.8 kcal mol^{-1} to 48.6 kcal mol^{-1} for the aziridine monosubstitution is fully justified as well as the minimal jump in the *DN* from the monosubstituted to the disubstituted phosphoramide. What it is not expected at all is the enormous post-correction *DN* value of 70.6 kcal mol^{-1} (91.5 kcal mol^{-1} before correction) for the tris(aziridinyl)-phosphine oxide or TEPA. The maximum *DN* we may expect from TEPA should be around 50 kcal mol^{-1}. The excess of enthalpy must be due to a side and undesired reaction. In fact, it is well known that aziridine ring is very prone to opening to give a linear ethyleneimine oligomer.[17] Considering that the reaction between TEPA and $SbCl_5$ was conducted in diluted conditions in an inert solvent (DCE), at relatively low temperature (25°C), it is reasonable to assume that on average only one aziridine ring per molecule has undergone the ring-opening reaction. When a three-terms ring is opened, the strain energy is released as enthalpy.[18] The strain energy of the aziridine ring is analogous to that of a cyclopropane ring.[19,20] Group increment thermochemical calculations although not highly refined, are reliable and were used also in recent research works.[21-23] For the ring opening of a three-terms ring Van Krevelen group increment approach suggests a release of a strain enthalpy of 23.9 kcal mol^{-1}.[18]

This enthalpy is the amount of heat that was released by the opening of an aziridine ring during the 1:1 adduct formation between TEPA and $SbCl_5$. Therefore, this enthalpy excess should be subtracted from the corrected *DN* value of TEPA reported in Table 1 (fourth column from right):

$$70.6\text{-}23.9 = 46.7 \text{ kcal mol}^{-1} \approx 50 \text{ kcal mol}^{-1} \quad (9)$$

yielding a corrected *DN* value for TEPA of 46.7 kcal mol^{-1} which can be rounded to 50 kcal mol^{-1}.

Table 2. Gutmann's solvent donor number (*DN*) in kcal mol^{-1}

Solvent or Donor Name	Gutman's *DN DN*	References and notes
1,2-dichloroethane	0	[1,7]
hexane	0	[1,7]
heptane	0	[1,7]
tetrachloromethane	0	[1,7]
benzene	0.1	[1,7]
toluene	0.1	[1,7]
thionyl chloride	0.4	[1,7]
dichloromethane	1	[1,7]
m-dichlorobenzene	2	[1,7]
carbon disulphide	2	[1,7]
benzoyl chloride	2.3	[1,7]
nitromethane	2.7	[1,7]
fluorobenzene	3	[1,7]
o-dichlorobenzene	3	[1,7]
bromobenzene	3	[1,7]
chlorobenzene	3.3	[1,7]
chloroform	4	[1,7]
iodobenzene	4	[1,7]
nitrobenzene	4.4	[1,7]
nitroethane	5	[1,7]
m-xylene	5	[1,7]
p-xylene	5	[1,7]
styrene	5	[1,7]
2-chloroethanol	5	[1,7]
furan	6	[1,7]
ethylbenzene	6	[1,7]
cumene	6	[1,7]
phenetole	8	[1,7]
anisole	9	[1,7]
monochloroacetonitrile	9.6	[1,7]
mesitylene	10	[1,7]
acetic anhydride	10.5	[1,7]
phenol	11	[1,7]
biacetyl	11	[1,7]
methyl propanoate	11	[1,7]
phosphorus oxychloride	11.7	[1,7]
benzonitrile	11.9	[1,7]
ethyl chloroacetate	13	[1,7]
acetonitrile	14.1	[1,7]
dioxane	14.8	[1,7]
sulfolane	14.8	[1,7]
3-pentanone	15	[1,7]
ethyl benzoate	15	[1,7]
acetophenone	15	[1,7]
butyl acetate	15	[1,7]
4-methyl-2-oxo-1,3-dioxolane	15.1	[1,7]
benzyl cyanide	15.1	[1,7]
propylene carbonate	15.1	[1,7]
i-butanenitrile	15.4	[1,7]
di(2-chloroethyl)ether	16	[1,7]
propyl acetate	16	[1,7]
benzaldehyde	16	[1,7]
methyl isobutyl ketone	16	[1,7]
diethyl carbonate	16	[1,7]
propanenitrile	16.1	[1,7]
methyl acetate	16.3	[1,7]
ethylene carbonate	16.4	[1,7]
butanenitrile	16.6	[1,7]

contg. Table 2.

2-propanone (acetone)	17	[1,7]
t-butyl-methyl ketone	17	[1,7]
ethyl propanoate	17.1	[1,7]
methyl i-propyl ketone	17.1	[1,7]
ethyl acetate	17.1	[1,7]
dimethyl carbonate	17.2	[1,7]
2 butanone	17.4	[1,7]
water	18	[1,7]
cyclopentanone	18	[1,7]
cyclohexanone	18	[1,7]
2-methyltetrahydrofuran	18	[1,7]
4-butyrrolactone	18	[1,7]
di-n-propyl ether	18	[1,7]
di-i-propyl ether	19	[1,7]
di-n-propyl ether	19	[1,7]
formic acid	19	[1,7]
methanol	19	[1,7]
glycerol	19	[1,7]
dibenzyl ether	19	[1,7]
diethyl ether	19.2	[1,7]
ethanol	19.2	[1,7]
butanol	19.5	[1,7]
propanol	19.8	[1,7]
tetrahydrofuran	20	[1,7]
acetic acid	20	[1,7]
1,2-ethandiol	20	[1,7]
1,2-dimethoxyethane	20	[1,7]
tetrahydrofuran	20	[1,7]
2-propanol	21.1	[1,7]
1,3-dioxolane	21.2	[1,7]
2-methyl-2-propanol	21.9	[1,7]
tetrahydropyran	22	[1,7]
2-phenylethanol	23	[1,7]
benzyl alcohol	23	[1,7]
trimethyl phosphate	23	[1,7]
tributyl phosphate	23.7	[1,7]
1,8-cineole	24	[1,7]
formamide	24	[1,7]
n-pentanol	25	[1,7]
triethyl phosphate	26	[1,7]
N,N-dimethylformamide	26.6	[1,7]
N-methylformamide	27	[1,7]
N,N-dimethylaniline	27	[1,7]
N-methylpyrrolidone (NMP)	27.3	[1,7]
N,N-dimethylacetamide	27.8	[1,7]
1,3 dimethylimidazolidin-2-one (DMEU)		[1,7]
n-butanol	29.0	[1,7]
$(NMe_2)(EtO)_2P=O$	29.5	This work revised from [15]
N,N,N',N'-tetramethylurea	29.6	[1,7]
dimethyl sulfoxide	29.8	[1,7]
methanol	30	[1,7]
n-propanol	30	[1,7]
n-hexanol	30	[1,7]
N,N-diethylformamide	30.9	[1,7]
o-chloroaniline	31	[1,7]

contg. Table 2.

n-decanol	31	[1,7]
dibutyl sulfoxide	31	[1,7]
quinoline	32	[1,7]
ethanol	32	[1,7]
isopentanol	32	[1,7]
n-octanol	32	[1,7]
N,N-diethylacetamide	32.2	[1,7]
3,4,5,6-tetrahydro-1,3-dimethylpyrimidin-2(1H)-one (DMPU)	33 ?	[1,7]
N-methylaniline	33	[1,7]
pyridine	33.1	[1,7]
4-methylpyridine	34	[1,7]
pyridine oxide	34.4	[1,7]
aniline	35	[1,7]
isopropanol	36	[1,7]
p-methypyridine N-oxide	36.3	[1,7]
$(NMe_2)_2(EtO)P=O$	36.4	This work revised from [15]
$(NEt_2)_3P=O$	36.6	This work revised from [15]
isobutanol	37	1,7
$(NMe_2)_2(NEt_2)_2P=O$	37.8	This work revised from [15]
n-butanol	38	[1,7]
$(NMe_2)_2$(pyrrolidino)P=O (MPPA)	38.0	This work revised from [15]
HMPA or HMPT	38.8	[1,7]
3-methylpyridine	39	[1,7]
dimethylsulphide	40	[1,7]
$(NEt_2)_2$(pyrrolidino)P=O	40.2	This work revised from [15]
$(NMe_2)(NHEt)_2P=O$	40.6	This work revised from [15]
$(piperidino)_3P=O$	40.9	This work revised from [15]
diethylsulphide	41	[1,7]
$(NMe_2)_2$(azetidino)P=O	41.1	This work revised from [15]
$(NMe_2)_2(NHEt)P=O$	41.2	This work revised from [15]
n-butylamine	42	[1,7]
$(NMe)_2(MeN\text{-}CH_2\text{-}CH_2\text{-}NMe)P=O$	42.1	This work revised from [15]
$(NMe_2)(azetidino)_2P=O$	42.3	This work revised from [15]
$(NEt_2)(pyrrolidino)_2P=O$	42.6	This work revised from [15]

contg. Table 2.

$(azetidino)_3P=O$	43	This work revised from [15]
t-pentanol	44	[1,7]
hydrazine	44	[1,7]
$(NMe_2)(pyrrolidino)_2P=O$ (DPPA)	45.4	This work revised from [15]
$(pyrrolidino)_3P=O$ (TPPA or TPPT)	47.2	This work revised from [15]
$(NHEt)_3P=O$	47.3	This work revised from [15]
$(NMe_2)_2$(aziridino)P=O	48.6	This work revised from [15]
$(NMe_2)(aziridino)_2P=O$	49.1	This work revised from [15]
diethylamine	50	[1,7]
tri-n-butylamine	50	[1,7]
$(aziridino)_3P=O$ (TEPA)	50	This work revised from [15]
piperidine	51	[1,7]
Trioctylamine N-oxide	52.3	[1,7]
ammonia	59	[1,7]
triethylamine	61	[1,7]

Thus, eq. 8 can be written as follows:

$(NMe_2)_3P=O$ → $(NMe_2)_2$(aziridino)P=O → $(NMe_2)(aziridino)_2P=O$ → $(aziridino)_3P=O$ (10)

[*DN*= 38.8] [*DN*= 48.6] [*DN*= 49.1] [*DN*≈ 50]

and now makes sense.

Conclusions

The available Gutmann Donor Number (*DN*) values for a series of phosphoramides were corrected by a correction factor 38.8/50.3, the ratio between the accepted *DN* value of HMPT and that found by Bollinger et al.[15] The selection of the correction factor is also supported by the comparison of the *DN* values of HMPT, MPPA and TPPT or TPPA measured by Bollinger et al.[15] and the experimental *DN* values measured by other authors.[16]

Only for TEPA it was necessary to consider a further correction of the *DN* value, since the value of 91.5 kcal mol^{-1} originally reported by Bollinger et al.[15], is affected by the systematic error and by a ring-opening reaction of about one aziridine ring per TEPA molecule. These considerations have led to the conclusions that TEPA has a high *DN* ≈ 50 kcal mol^{-1} but not the extraordinary high and unexplainable of 91.5 kcal mol^{-1}.

In Table 2 are reported the *DN* values of 162 different solvent molecules including all the revised values of phosphoramides. From this table it is possible to observe that all the phosphoramides considered are characterized by the highest *DN* values among all the solvents considered, but their values are not at all extraordinarily high as it was thought in the past. TEPA has a *DN* value similar to certain amines like diethylamine, tributylamine and piperidine.

It is also interesting the following regularity which is linked to the number of terms in the heterocyclic rings:

(aziridino)$_3$P=O *DN* = 50 kcal mol^{-1}

(azetidino)$_3$P=O *DN* = 43 kcal mol^{-1}

(pyrrolidino)$_3$P=O *DN* = 47.2 kcal mol^{-1}

(piperidino)$_3$P=O *DN* = 40.9 kcal mol^{-1}

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