Nuclear Magnetic Resonance Investigation of Geometrical Isomerism in the Anions of Aromatic Amino Compounds. "Effective Size" of a Lone Electron Pair

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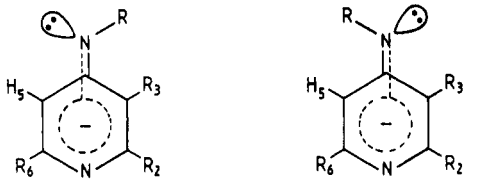
The ^1H and ^{13}C NMR spectra of the anions of 4-, 3-, and 2-aminopyridine, 4-aminopyrimidine, and some of their methyl derivatives in liquid ammonia containing potassium amide at −50 °C are measured, and their signals are assigned to the syn and the anti isomers. The influence of an *o*-methyl substituent on the isomer ratio gives an indication for the "effective size" of the nitrogen lone electron pair, which in these anions appears to be larger than the hydrogen in the NH^- group. Comparison of the ^{13}C NMR spectra with those of (methylamino)pyridines reveals a great difference in the effect of the orientation of the NH^- and of the NCH_3^- group on the chemical shifts of the ortho carbon atoms. In the aminopyridine anions the carbons syn with respect to the nitrogen lone pair resonate at higher field than in the anti position, whereas in the (methylamino)pyridine anions a reversed relationship was found.

A recent NMR spectroscopic study of the anions of some aromatic amino compounds in liquid ammonia containing potassium amide at −50 °C has unequivocally proved the occurrence of geometrical isomerism in these systems.[1] This phenomenon has been ascribed to an enhanced double bond character of the exocyclic carbon–nitrogen bond, leading to restricted rotation. From a ^1H and ^{13}C NMR study of the anions of 2-, 3-, and 4-(methylamino)pyridines, allowing the assignment of the syn and anti isomers,[2] it appeared that the ortho hydrogen and carbon atoms syn oriented to the electron pair of the methylamino group all resonate at a lower field than the hydrogen and carbon atoms in the anti position. In continuation of this work we studied the ^1H and ^{13}C NMR spectra of the anions of 4-, 3-, and 2-aminopyridine and some of their *C*-methyl derivatives and established the assignment of the signals to either the syn or the anti isomer.

Results and Discussion

(A) 4-Aminopyridines. Different signals appear for all aromatic hydrogen atoms in the ^1H NMR spectra of the anions of 4-aminopyridine (**1**) and 4-amino-2,6-dimethylpyridine (**2**), measured in liquid ammonia containing po-



	R	R_2	R_3	R_6
1:	H	H	H	H
2:	H	CH_3	H	CH_3
3:	H	H	CH_3	H
4:	CH_3	H	H	H

tassium amide at −50 °C (Table I). The nonequivalency of H-3 and H-5 and of H-2 and H-6 is a result of restricted rotation around the exocyclic carbon–nitrogen bond. Geometrical isomers are also observed for the anion of 4-amino-3-methylpyridine (**3**), as appears in the ^1H NMR spectra from two signals for each H-2, H-5, and H-6 (Table I). The isomeric ratio is, of course, 50:50 for anions **1** and **2** due to their symmetry; for anion **3** an isomeric ratio of 75:25 is found (determined by integration of appropriate proton signals), showing that a methyl substituent in an ortho position to the NH^- group has a considerable influence on the isomer distribution.[1] When the solution containing **3** [3] was allowed to stand for 1 day at room temperature in a sealed tube, the spectrum did not change. This shows that the syn and anti isomers of **3** are in thermodynamic equilibrium. To decide which signals belong to the syn or anti structure of the anions, we used both ^1H and ^{13}C NMR spectroscopic data (Tables I and II) and applied two criteria for discerning these structures. The first one is the well-known dependence of the coupling constant $^3J_{^{13}C-NH}$ on the geometry of the system.[3] When the $^3J_{^{13}C-NH}$ between the hydrogen of the anionic amino group and the carbon atom in ortho position was used, the coupling constant is larger for the anti than for the syn structure.[3] The second criterion is the chemical shift of the ortho hydrogens. In a previous paper it was unequivocally established that an ortho hydrogen, being in a position syn relative to the lone pair of an anionic methylamino group, is more deshielded than in the anti position and thus appears at lower field.[2] We can use this result in the aminopyridine anions, since the shielding of the ortho hydrogen in these anions will be primarily determined by electric field effects caused by the lone-pair orientation and to a lesser extent by the NH or NCH_3 group.[4] On consideration of the spectra of anion **3**, we observed that in the predominant isomer $^3J_{^{13}C-NH}$ for C-5 is larger (15 Hz, Table II) than that for the minor isomer (8 Hz); moreover, H-5 in the major isomer resonates at lower field (Table I). On the basis of these two criteria, we reached the conclusion that isomer **3a** is the predominant one. This result seems to indicate that the "effective size" of the electron pair on the NH^- group is *larger* than that of the hydrogen atom of NH^-, leading to a preference for **3a** in which the proton is near the *o*-methyl substituent. This is a somewhat surprising result, since the sp^2 electron pair in pyridine and comparable compounds[5-7] as well as

(1) Kos, N. J.; Breuker, J.; van der Plas, H. C., van Veldhuizen, A. *Heterocycles* **1981**, *15*, 1041.
(2) Kos, N. J.; Breuker, J.; van der Plas, H. C.; van Veldhuizen, A. *J. Org. Chem.* **1981**, *46*, 3509.
(3) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1978.
(4) The term "lone pair" is used for the two electron pairs on the amino nitrogen atom. While the formulas used throughout this paper might suggest an sp^2 lone pair, with a p orbital in conjugation with the pyridine ring, we realize that this is only an approximation, since the negative charge is not fully delocalized in the aromatic ring.

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Table I. ^{1}H NMR Data of the Anions of Aminopyridines and Aminopyrimidines in Liquid Ammonia Containing Potassium Amide at −50 °C[a,b]

anion of	compd no.	chemical shift H-2	H-3	H-4	H-5	H-6	CH_3	NH	isomer distribution, %
4-aminopyridine	1a	7.26	5.66		5.82	7.18		4.00	50:50
4-amino-2,6-dimethylpyridine	2a		5.46		5.62		1.91, 1.95	3.86	50:50
4-amino-3-methylpyridine	3a	7.22			5.89	7.27	7.27	3.84	75
	3b	7.20			5.64	7.14	1.79	4.12	25
4-(methylamino)pyridine	4a	7.43	5.60		5.89	7.22	2.54		
	5a	7.21		6.20	6.39	6.70		3.19[c]	60
	5b	7.39		6.03	6.47	6.70		3.15[c]	40
3-amino-6-methylpyridine[13]	6a	7.15		6.16	6.24[c]		2.03	2.92	60
	6b	7.32		6.00	6.33[c]		2.03	2.84	40
3-amino-2-methylpyridine	7a			6.23	6.47[c]	6.71	2.02	2.90	70
	7b			5.96	6.39[c]	6.65	2.02	3.33	30
3-amino-4-methylpyridine	8a	7.15			6.40	6.69	1.87	3.32	35
	8b	7.41			6.45	6.74	1.82	2.92	65
3-(methylamino)pyridine	9a	7.03		*d*	*d*	6.84	2.60		20
	9b	7.50		5.76	*d*	*d*	2.50		80
2-aminopyridine	10a		5.73	6.70	5.49	7.45		3.90	55
	10b		5.82	6.62	5.42	7.32		4.22	45
2-amino-5-methylpyridine	11a		5.70	6.55		7.25	1.85	3.7	55
	11b		5.82	6.52		7.12	1.85	4.0	45
2-amino-3-methylpyridine	12a			6.68	5.51	7.42	1.79	3.74	70
	12b			6.55	5.40	7.23	1.79	4.39	30
2-(methylamino)pyridine	13a		5.58	6.96	5.57	7.57	2.54		60
	13b		5.81	6.57	5.35	7.50	2.62		40
4-aminopyrimidine	14a	7.67			5.81	7.24		4.80	70
	14b	7.82			5.78	7.24		4.74	30
4-amino-6-methylpyrimidine	15a	7.54			5.58		1.83	4.73	70
	15b	7.70			5.52		1.83	4.53	30
4-amino-6-phenylpyrimidine	16a	7.76			6.34			5.05	75
	16b	*e*			6.26			4.95	25

[a] Chemical shifts relative to Me_4Si (δ 0). [b] Coupling constants: $J_{2,3}$ = 6 Hz, $J_{2,4}$ = 3 Hz, $J_{3,4}$ = 8–8.5 Hz, $J_{3,5}$ = 1.5–2.5 Hz, $J_{4,5}$ = 6–8 Hz, $J_{4,6}$ = 1.5–2.5 Hz, $J_{5,6}$ = 4–6 Hz. [c] These assignments may also be interchanged. [d] Present as a complex signal between 6.4 and 6.7 ppm. [e] In same region as the phenyl signals.

Table II. ^{13}C NMR Data of Aminopyridines and *N*-(Methylamino)pyridines in $CDCl_3$ at 35 °C and of Their Anions in Liquid Ammonia Containing Potassium Amide at −50 °C[a]

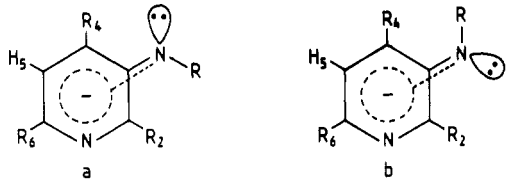
compd	type	chemical shift C-2	C-3	C-4	C-5	C-6	CH_3	$^3J_{^{13}C-NH}$, Hz
4-aminopyridine	neutral[20,b]	149.6	109.8	156.3	109.8	149.6		
	anion 1a	148.1[c]	112.9	168.6	111.0	148.4[c]		5 (C-3), 13 (C-5)
4-amino-2,6-dimethylpyridine	neutral	158.5	106.5	153.7	106.5	158.5	24.4	
	anion 2a	154.4[c]	108.7	169.1	106.6	154.8[c]	24.0, 24.2	8 (C-3), 15 (C-5)
4-amino-3-methylpyridine	neutral	150.3	117.0	151.8	109.1	148.3	14.0	
	anion 3a	*d*	116.4	166.7	110.3	*d*	15.6	15 (C-5)
	anion 3b	*d*	117.9	166.8	111.3	*d*	16.5	8 (C-5)
4-(methylamino)pyridine	neutral	149.8	107.3	154.9	107.3	149.8	29.2	
	anion 4a	149.5	102.4	163.0	115.0	146.1	36.5	
3-amino-6-methylpyridine[13]	neutral	136.9	140.3	122.8	123.3	148.3	23.3	
	anion 6a	138.3	159.8	118.2	123.2	130.3	22.3	13 (C-4)
	anion 6b	137.6	160.0	120.0	123.2	130.3	22.3	8 (C-4)
3-(methylamino)pyridine	neutral	135.5	146.0	118.1	124.0	137.7	30.0	
	anion 9a	129.5	159.2	123.0	122.3	125.1	37.3	
	anion 9b	143.6	159.2	107.4	124.8	122.6	37.3	
2-aminopyridine	neutral[21,e]	160.5	108.5	136.8	111.7	147.8		
	anion 10a	172.7	112.9	134.9	100.4	149.5		6 (C-3)
	anion 10b	171.2	111.2	134.7	99.9	149.0		13 (C-3)
2-amino-5-methylpyridine	neutral[21,e]	158.3	108.4	138.0	121.0	147.4	17.1	
	anion 11a	171.5	112.6	136.3	107.4	148.2	17.2	small (C-3)
	anion 11b	170.2	110.8	136.3	106.8	147.8	17.2	13 (C-3)
2-(methylamino)pyridine	neutral	160.0	106.3	137.6	112.7	148.2	29.0	
	anion 13a	166.7	114.5	132.2	99.1	149.1	35.5	
	anion 13b	168.6	102.0	136.2	100.1	149.6	36.6	
4-aminopyrimidine	neutral[22,f]	158.3		163.2	105.1	154.6		
	anion 14a	159.2		169.0	108.6	150.2		12 (C-5)
	anion 14b	159.8		171.1	110.0	150.1		7 (C-5)

[a] Chemical shifts relative to Me_4Si (δ 0). [b] Measured in ethanol. [c] These assignments may be interchanged. [d] A complex spectrum is found at 146.6–147.1 ppm. [e] Measured in hexamethylphosphoramide. [f] Measured in dimethyl sulfoxide.

the sp^3 electron pair in, for instance, piperidine[8] is found to be "smaller" than a hydrogen atom. In the anions investigated in this study, however, two distinct differences have to be taken into consideration in comparison with the systems mentioned in the literature: (i) in liquid ammonia solvation takes place and probably makes the electron pair effectively larger than a hydrogen,[9] (ii) we are dealing with an electron pair in an anionic amino group, and theoretical calculations have shown that the size of an electron pair increases strongly in the series NH_3, NH_2^-, NH^{2-}.[10] It cannot be excluded that isomer **3a** is better solvated than isomer **3b**, since solvation of the electron pair in **3b** may be hindered by the *o*-methylsubstituent, leading to destabilization. A complication also arises from the possibility that there is an electronic preference for one of the isomers.[11] It is interesting to notice that the coupling constants $^3J_{^{13}C-NH}$ for C-5 of **3a** (15 Hz) and **3b** (8 Hz) are not smaller than those for C-3 and C-5 of **1** and **2** (Table II). $^3J_{^{13}C-NH}$ strongly depends on the configuration and will be sensitive to rotation of the amino group.[3] Apparently the *o*-methyl substituent is not able to push the amino group out of the plane of the aromatic ring.[12] The same two criteria as mentioned above are used for the interpretation of the ^1H and ^{13}C NMR signals of the anions **1** and **2** (Tables I and II).

The assignments of the signals for C-2 and C-6 in both anions are not completely certain and may ultimately have to be reversed. Comparison with the spectra of **3** did not make a definitive assignment of C-2 and C-6 possible either. Comparison of the ^{13}C NMR spectra of the now firmly established structures **1a**, **2a**, and **3a** with that of the anion of 4-(methylamino)pyridine (**4a**, Table II) showed the interesting feature than in **4a** the signal of the ortho carbon atom anti relative to the lone pair (C-3) is found at higher field than C-5,[2] while in **1a**, **2a**, and **3a** the higher field signal has to be ascribed to the carbon atom in the syn position (C-5). The anomalous behavior of C-3 may be due to steric compression in **3a**.

(B) 3-Aminopyridines. In the ^1H NMR spectrum of the anion of 3-aminopyridine (**5**) two isomers can be discerned in a ratio 60:40. We applied the same two criteria as mentioned in section A for the signal assignment of the hydrogens in the two isomeric configurations (**5a** and **5b**). Since establishment of the magnitude of the $^3J_{^{13}C(4)-NH}$ is disturbed by coupling of C-4 with H-6, we measured $^3J_{^{13}C(4)-NH}$ in the anion of 3-amino-6-methylpyridine (**6**).[13] Anion **6** gives the same isomeric ratio as **5**, i.e., 60:40. Application of the two criteria gives the following results for the more abundant isomer of **6** (Tables I and II): (i) $^3J_{^{13}C-NH}$ for C-4 is 13 Hz and smaller for C-2; (ii) the ortho H-4 is observed at lower field than H-4 in the minor isomer. These results lead to the conclusion that isomer **6a** is predominant over **6b**. This is confirmed by the chemical shift of H-2, which lies further upfield in **6a** than H-2 in **6b**, and the magnitude of $^3J_{^{13}C-NH}$ of the less abundant isomer, being 8 Hz for C-4. The same result is obtained for **5**.



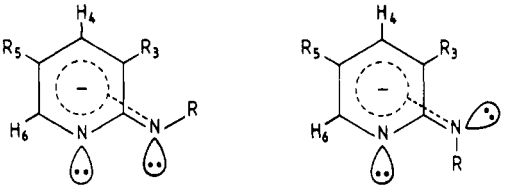
a b

	R	R_2	R_4	R_6
5:	H	H	H	H
6:	H	H	H	CH_3
7:	H	CH_3	H	H
8:	H	H	CH_3	H
9:	CH_3	H	H	H

The chemical shifts of H-4 in the anion of 3-amino-2-methylpyridine (**7**) show that the preferred isomer has conformation **a**. The isomer ratio has slightly changed in favor of structure **a** (70:30). Thus, it is evident that the presence of a methyl group at position 2 promotes the formation of configuration **a**. On the basis of the chemical shift of H-2 in the anion of 3-amino-4-methylpyridine (**8**, Table I), being at lower field in the more abundant isomer, **8b** is the favored isomer. From these results it is evident that a methyl substituent ortho to the anionic amino group causes a preference for the isomer in which the amino hydrogen is directed to the methyl group. This indicates that the steric requirement of the electron cloud on the anionic amino group can be considered as "effectively larger" than the amino hydrogen. This conclusion is in agreement with the one reached in section A.

On consideration of the ^{13}C NMR spectra of anion **6**, it appears that the carbon atom syn to the lone pair (C-4, $^3J_{^{13}C-NH}$ = 13 Hz) resonates at higher field than C-4 in the anti position ($^3J_{^{13}C-NH}$ = 8 Hz). An analogous difference is observed for C-2. When we compare this result with that of our previous study concerning the anion of 3-(methylamino)pyridine (**9**), we see that this relationship is reversed: both in **9a** and **9b** the ortho carbon atoms syn to the lone pair are found further downfield than those in the anti position.[2] In section A an analogous difference between 4-aminopyridine and 4-(methylamino)pyridine was found. A second interesting difference between **5** and **9** concerns the isomer ratio. Anion **9** exists mainly (80%) in the configuration **b**, whereas for **5** structure **a** is predominant.

(C) 2-Aminopyridines. We have already reported that the anion of 2-aminopyridine (**10**) exists in two isomeric forms (ratio 55:45).[1] This ratio was shown to be independent of the concentration of both **10** and potassium amide.[1] To facilitate the determination of $^3J_{^{13}C-NH}$ we



a b

	R	R_3	R_5
10:	H	H	H
11:	H	H	CH_3
12:	H	CH_3	H
13:	CH_3	H	H

(5) Almog, J.; Meyer, A. Y.; Shanan-Atidi, H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 451.
(6) Nasipuri, D.; Konar, S. K. *J. Chem. Soc., Perkin Trans. 2* **1979**, 269.
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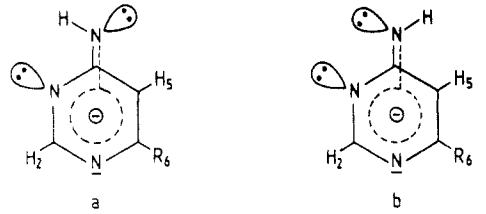
(10) Robb, M. A.; Haines, W. J.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1973**, *95*, 42.
(11) It seems possible that hyperconjugation with the methyl group can lead to more stabilization in **3a** (trans configuration) than in **3b**.
(12) Only a little steric hindrance is supposed to be present in 3-methyl-4-(dimethylamino)pyridine (Proba, Z.; Wierzchowski, K. L. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1119).
(13) For uniformity **7** is considered as 3-amino-6-methylpyridine instead of 5-amino-2-methylpyridine.

measured the ^{13}C NMR spectrum of the anion of 2-amino-5-methylpyridine (**11**). The isomeric forms of **11** are present in the same ratio as those in **10**. For the syn–anti assignment we again used the same two criteria as discussed already, i.e., $^3J_{^{13}C-NH}$ for C-3 and the chemical shift difference of H-3. The results shown in Tables I and II led to the conclusion that conformer **10a**, in which the two electron pairs are in the syn orientation, is slightly preferred, although by repulsion of the electron pairs on the two nitrogen atoms and intramolecular hydrogen bonding[14] **10b** would be expected to be favored. The observed predominancy of **10a** may be ascribed to stabilization as a result of complexation of the potassium cations with both lone pairs. Some evidence for this hypothesis was obtained from the observation that the amount of **10a** decreases and even disappears in favor of **10b** on addition of 18-crown-6 ether, a compound known to form complexes with potassium cations. Using cesium amide instead of potassium amide also slightly favors **10b** (ratio 35:65). These results are analogous to the behavior of the anion of 2-(methylamino)pyridine (**13**). The syn–anti assignment in the anion of 2-amino-3-methylpyridine (**12**) cannot be based on the position of a hydrogen atom ortho to the amino group, but comparison of the chemical shifts of H-4, H-5, and H-6 in the anions **10**–**12** indicates that the predominant structure is **12a**. This is confirmed by the change in isomeric ratio in favor of **12b**, when 18-crown-6 ether is used or cesium amide is added instead of potassium amide. The preference for **12a** is stronger (70:30) than that for **10a** and **11a** (55:45) and does not alter when the temperature is allowed to rise to 20 °C. This result can again be explained in terms of the electron pair being "larger" than a hydrogen atom. Considering the position of the C-3 signal in the ^{13}C NMR spectrum of anions **10** and **11**, it is evident that this ortho carbon atom in the syn position relative to the lone pair ($^3J_{^{13}C-NH}$ = 13 Hz) is observed at higher field than that in the anti position ($^3J_{^{13}C-NH}$ = 6 Hz). In anion **13** this relationship is reversed. This is an agreement with the results in sections A and B.

(D) 4-Aminopyrimidines. We have already reported that the anion of 4-aminopyrimidine (**14**) gives two isomeric conformations in the ratio of 70:30 (Table I).[1] This ratio does not change on standing at room temperature for an hour, so we are dealing with a thermodynamic equilibrium. We can use the signals of H-5 and C-5 and $^3J_{^{13}C-NH}$ for the syn–anti assignment. In the more abundant isomer H-5 appears at lower field and C-5 at higher field, while $^3J_{^{13}C-NH}$ is 12 Hz compared with 7 Hz for the other isomer, showing that **14a** is the predominant isomer. This conclusion is further substantiated by the observation that on addition of 18-crown-6 ether the signals of the minor isomer **14b**, which is probably stabilized by complexation with the potassium cation, disappear. When cesium amide is used instead of potassium amide we also find less of **14b**.



a b

14: R_6 = H
15: R_6 = CH_3
16: R_6 = C_6H_5

It is evident from the ^1H NMR spectra of the anions of 4-amino-6-methylpyrimidine (**15**) and 4-amino-6-phenylpyrimidine (**16**) that these anions are preferably present in conformation **a** as well (Table I). Apparently a methyl or phenyl group in position 6 does not significantly influence the isomer ratio.

The interesting fact that the anions **14**–**16** prefer the isomeric form in which the two electron pairs are in the anti orientation, while the anion of 2-aminopyridine (**10**) slightly prefers the syn structure, is possibly caused by a different delocalization pattern of the negative charge. This may be due to the fact that in 4-aminopyrimidine (**14b**) a part of the negative charge is present on the para ring nitrogen atom. This decreased electron density on N-3 and on the NH^- group may cause a less efficient complexation of the potassium cation.[15] As a result, hydrogen bonding [14] and mutual repulsion of the electron pairs will favor **14a**.

Conclusion

It is evident from this study that an electron pair is "larger" than a proton on an NH^- group, but this result cannot be completely ascribed to steric factors. It is possible that the preferred isomer is also favored by better solvation than the other isomer, and a difference in electronic stabilization may also exist. The results are complicated further by the fact that there are two lone pairs present on the NH^- group which will both have some conjugation with the aromatic ring.

This study clearly shows that, in contrast to what has been observed with the anions of the methylaminopyridines, the carbon atom in the syn orientation to the lone pair appears at higher field than the corresponding carbon in the anti position. As the chemical shifts of the syn carbon atoms in the methylaminopyridines are predominantly determined by steric compression,[2] it is evident that other factors working in an opposite direction are involved here.

Experimental Section

The procedures followed to obtain the ^1H and ^{13}C NMR spectra have been described previously.[1] All compounds were commercially available or synthesized according to known procedures (4-amino-2,6-dimethylpyridine,[16] 4-amino-3-methylpyridine,[17] 5-amino-2-methylpyridine,[18] 3-amino-2-methylpyridine,[18] 3-amino-4-methylpyridine,[18] 4-amino-6-methylpyrimidine,[19] and 4-amino-6-phenylpyrimidine[19]).

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Registry No. **1**, 37062-09-2; **2**, 80287-50-9; **3**, 80287-51-0; **4**, 77862-17-0; **5**, 80287-52-1; **6**, 80287-53-2; **7**, 80287-54-3; **8**, 80287-55-4; **9**, 77862-20-5; **10**, 41458-22-4; **11**, 37062-15-0; **12**, 65032-12-4; **13**, 77862-22-7; **14**, 65626-52-0; **15**, 80287-56-5; **16**, 80293-83-0.

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