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DICATION ETHERS - 10. ¹ STABLE DIPOLES FROM A BIS-ACRIDINIUM ETHER SALT AND CYCLIC &-DIKETONATES

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Abstract - 9,9'-Oxy-bis(10-methylacridinium) bis(trifluoromethanesulfonate) reacts with cyclic &-diketonates by nucleophilic substitution to give deeply colored 2-acridinio-1,3-diketonates. These stable dipoles exhibit pronounced negative solvatochromism. Linear correlations between the transition energy of the solvatochromic absorption maximum and the $E_T(30)$ as well as Z values of different solvents are found.

The ambident reactivity of β -diketonates allows an electrophilic attack either at a carbon or an oxygen atom of the ambident anion.² In the course of our work with dication ether salts, we have noticed that the ambidoselectivity depends on the dication ether salt used. With bis-formamidinium ether or bis-pyridinium ether salts, O-attack leading to an O-formamidinium- (or O-pyridinium-) substituted β -ketoenol occurs except when the β -diketonate is the anion of a malonic ester or of Meldrum's acid.^{3,4}

In contrast, bis-acridinium ether <u>la</u> reacts with B-diketonates under C/C bond formation in all cases (Scheme 1). The reactions were carried out with the methylene compounds <u>2a-i</u> in the presence of a polymer-supported tertiary amine. With cyclic B-diketonates <u>2a-b</u>, the deeply colored betaines <u>3a-b</u> are formed in an addition/elimination reaction. With the anion of dibenzoylmethane, on the other hand, the yellow olefin <u>5</u> is obtained. The same substitution reaction as on <u>la</u> can be carried out on the 10-methyl-9-trifloxyacridinium salt <u>1b</u>, as has been shown with <u>2a</u> and <u>2i</u>. Actually, <u>1b</u> is to be preferred over <u>la</u> as starting material, because in the latter case, a molar equivalent of acridinone <u>4</u> is lost in the nucleophilic displacement reaction. However, syntheses with <u>1a</u> may have model character for the réactivity of other dication ether systems whose related trifloxy carbenium salts cannot be isolated, but are merely intermediates in the synthesis of the dication ether (e.g. bis-tropenylium ether, substituted bis-cyclopropenylium ethers).⁵

The dipolar character of 3a-h and the olefinic structure of 5 follow from spectral data. In the ¹H NMR spectrum, the N-Me signal appears at δ 4.5-4.8, which is close to the value found in N-me-thylacridinium triflate (δ 4.94 in nitromethane ⁶). In contrast, the N-Me resonance of 5 is registered at δ 3.63, similarly to 10-methyl-9(10H)-acridinone (δ 3.70 in chloroform ⁶).

In the infrared spectrum of 5, the C=O absorption (1662 cm⁻¹) is in the range expected for an α , B-unsaturated ketone, whereas the B-diketonate units in 3a, c, f, g absorb at distinctly lower wavenumbers. In 3b and 3h, the additional keto functions not involved in the delocalization of negative charge give rise to absorptions around 1690 cm⁻¹. Similarly, the values of \tilde{v} = 1666 (1662) cm⁻¹ for the α -pyrone derivatives 3d and 3e have to be attributed to the ester carbonyl stretching vibration; these values are some 35 wavenumbers lower than for the precursors 2d and 2e which exist

as 4-hydroxy-a-pyrone derivatives.



The different bond structure of compounds 3 and 5 clearly arises from the fact that the cyclic 8-diketonate moiety is constrained to a planar, W-shaped configuration. Because of severe steric hindrance between this unit and the <u>peri-hydrogens</u> of the acridine system, coplanarity of both structural subunits is precluded, forcing 3 to exist with the subunits perpendicular (or nearly perpendicular) to each other. In 5, on the other hand, charge compensation with formation of an exocyclic double bond becomes possible by rotation around the two =C-C=O single bonds which removes the close proximity between keto groups and <u>peri-hydrogens</u>.

The electronic absorption spectra of betaines 3a-b (Table I) all show three maxima ($\lambda = 253-260$, 344-361, 413-424 nm), which are typical for the acridinium system, 6,7 and a strongly solvatochromic

long-wavelength absorption. Hypsochromic shifts of the latter absorption are observed in all cases when the solvent polarity is increased (negative solvatochromism); this corresponds to enhanced stabilization of the dipolar ground state of the betaines in more polar solvents. For example, the UV/VIS spectra of 3a in several solvents are depicted in Fig. 1. It will be noted, that there is no longer a distinct maximum for the solvatochromic absorption, when 3a is dissolved in water. A closer inspection, however, reveals a poorly defined shoulder on the long-wavelength side of the 419 nm absorption, approximately at 490 nm. Log ε at this wavelength is only 3.22, much lower than for the solvatochromic absorption maxima in the other solvents. Because of the basicity of betaines 3, the same question arises as with merocyanine dyes, ^{8,9} namely whether this absorption is caused by an 0-protonated betaine or by a hydrogen-bonded betaine/water complex.

Table I. UV/VIS absorption maxima of 3a-h and 5 in various solvents at 23°C. Given are λ_{max} [nm] and log ε (in parentheses). ^a

compound	pyridine b	acetone	solvent acetonitrile	ethanol	methanol	water
3.9	635(3,62)	632(3,63)	615(3.55)	524(2,25)	512(2,21)	
**	422(3,59)	417(3 59)	418(3,60)	418(3.61)	418(3,62)	419(3.67)
	400(3.56)	397(3,60)	410(0.00)	410(3.01)	410(3.02)	419(3.07)
	349(4.02)	344(4.05)	345(4 26)	358(4 16)	358(4.09)	359(4 33)
	5.5(514(1105)	256(4.96)	259(4.91)	257(5.04)	259(4.95)
			230(4,30)	233(4.31)	257(5.04)	200(4.00)
3b	607(3.83)	597(3.82)	588(3.70)	534(3.60)	532(3.57)	479(3.49)
	420(3.57)	417(3.57)	416(3.49)	415(3.56)	415(3.51)	422(3.58)
	360(4.11)	356 4.11)	356(4.08)	359(4.25)	358(4.25)	359(4.37)
			257(4.88)	256(4.85)	257(4.88)	252(4,77)
3c	635(3,57)	628(3,63)	606	532	520(3.35)	
~	426(3.78)	421(3,90)	419	419	416(4.02)	
	346(4.24)	346(4.33)	348	357	358(4.46)	
	335(4.23)	333(4.33)	334	339	339(4.42)	
			259	260	259(5.04)	
34	593(3 69)	587(3.64)	582(3.61)	510(3.43)	492(3.45)	6
~	422(3,60)	419(3.57)	415(3.66)	420(3.64)	413(3,63)	425(3 66)
	356(4,18)	354(4.08)	355(4 14)	360(4 19)	360(4 24)	360(4,31)
	550(1110)	554(4100)	258(4,84)	257(4.87)	257(4.80)	253(4.96)
			250(1101)	257(1107)	237(4100)	233(4.90)
3e	582(3.64)	578	559(3.42)	502	490(4.43)	с
~~	424(3,94)	413	418(3.46)	419	422(3,62)	422
	359(4.15)	350	355(4.05)	360	361(4.24)	361
			259(4.76)	259	259(4,89)	258
3f	638(3.70)	629(3.69)	612(3,63)	529(3,41)	518(3,39)	с
~	424(3.67)	420(3.67)	420(3.68)	420(3.70)	420(3.71)	419
	353(4,15)	355(4,10)	354(4.17)	357(4.21)	358(4,20)	359
			305(4.11)	300(4.13)	296(4.14)	296
			259(4.80)	259(4.94)	259(4.92)	258
30	648(3,74)	642(3,63)	613(3,62)	529(3.41)	522(3,39)	c
~	424(3,67)	419(3,59)	419(3,59)	419(3,70)	419(3,71)	421
	357(4,12)	354(3,95)	355(4,10)	358(4.24)	358(4.24)	360
	310(4,13)	325(3.88)	305(4.05)	296(4.09)	293(4,17)	293
		••••	258(4,91)	256(5.00)	256(4,98)	258
35	589(3.64)	577(3.56)	561(3.46)			
~	422(3.85)	423(3 83)	421(3.40)	425 (3 86)	422(3 83)	425
	357(4 13)	353(4.10)	355(4 10)	360(4, 26)	360(4 24)	360
	337(4,13)	333(4.10)	259(4.91)	260(5.07)	259(5.07)	259
r		(20(0,00))				
2	430(3,83)	429(3.82)		(3, 39)	284(3.44)	
				43/(3./4)	419(3.09)	
				256(4 21)	257(4,/3)	
				200(4.21)	237(4.14)	

^a Because of extremely low solubility, the concentration of some solutions, and hence log ε values, could not be determined.

^b Absorption by the solvent prevents observation of shortest-wavelength maxima.

^c See text for the position of this absorption.

Table II. Transition energies (E_{T}) of the solvatochromic absorption maximum in betaines 3a-hand correlations with $E_{\tau}(30)$ and Z values

	с ₅ н ₅ N	(сн ₃) ₂ со	сн _з си	с ₂ н ₅ он	сн _з он	н ₂ 0
$E_{T}(30)$ value ^a	40.2	42.2	46.0	51.9	55.5	63.1
Z value b	64.0	65.5	71.3	79.6	83.6	94.6
E _T [kcal mol ⁻¹]	c and correl	ations:				
3a	45.0	45.2	46.5	54.6	55.8	
		$E_{T} = 0.798 E_{T}(30) + 11.8$			(n=5; r=0.967)	
		$E_{T} = 0.602 Z$	+ 5,6		(n=5; r=0.972)	
<u>3b</u>	47.1	47.9	48.6	53.5	53.7	59.7
		$E_{T} = 0.546 E$	(30) + 24.6		(n=6; r=0.984)	
		$E_{T} = 0.405 Z$	+ 20.8		(n=6; r=0.986)	
3c	45.0	45.5	47.2	43.7	55.0	
		$E_{T} = 0.719 E$	T(30) + 15.4		(n=5; r=0.982)	
		$E_{\rm T} = 0.542 {\rm z}$	+ 9.9		(n=5; r⇔0.986)	
3d	48.2	48.7	49.1	56.1	58.1	
		е _т = 0.700 е	$T^{(30)} + 19.0$		(n=5; r=0.964)	
		$E_{T} = 0.526 Z$	+ 13.7		(n=5; r=0.966)	
3e.	49.1	49.5	51.1	57.0	58.3	
		$E_{\rm T} = 0.660 {\rm E}$	T ⁽³⁰⁾ + 21.9		(n=5; r=0.982)	
		$E_{T} = 0.497 Z$	+ 16.8		(n=5; r=0.987)	
<u>,3£</u>	44.8	45.5	46.7	54.0	55.2	
		$E_{T} = 0.749 E_{T}$	T ⁽³⁰⁾ + 13.9		(n=5; r=0.975)	
		$E_{T} = 0.564 Z$	+ 8.2		(n=5; r=0.979)	
3g ∼∼	44.1	44.5	46.6	54.0	54.8	
		E _T = 0.789 E	$T^{(30)} + 11.6$	(n=5; r=0.977)		
		$E_{T} = 0.596 Z$	+ 5.4		(n=5; r=0.984)	
3h	48.5	49.5	51.0			

^a From ref. 10. - ^b From ref. 13. - ^c $E_T = h c N_A / \lambda_{max} = 2.859 \cdot 10^4 / \lambda_{max}$ [nm].

We have therefore synthesized salt $\frac{6}{2}$ by 0-protonation of $\frac{3}{2}$ with triflic acid. Its electronic spectrum in acetonitrile shows no maxima above 422 nm. This band, after a shoulder at \approx 440 nm which is typically found in acridinium systems, ⁶ descends steeply without the additional shoulder described above for 3a in water. Upon addition of 0.1 % NEt3, the solvatochromic absorption maximum at 615 nm appears. Spectra of 6 in water or in 0.1 N NaOH, or of 3a in 0.1 N NaOH, all show the weak shoulder at pprox 490 nm. A solution of 6 in aqueous triflic acid (1%), on the other hand, gives a longest-wavelength absorption which is very similar in shape to $\epsilon_{
m c}$ in acetonitrile. From these observations, it follows that the additional shoulder observed for 3 or 6 $\,$ in water does not correspond to the O-protonated betaine. Similar behavior in water as for 3a is also noticed for some of the other betaines; in the remaining ones, the solvatochromic absorption in water may be too weak and too broad to be recognized. Only for 3b, a distinct maximum is found (see Table I).



Fig. 1. Electronic absorption spectrum of 3a in different solvents.



The solvatochromic absorption maximum of betaines 3, like that of other betaine dyes, ¹⁰⁻¹² may be regarded as arising from an intramolecular charge transfer. Its transition energies in the different solvents give satisfactory linear correlations (Table II) with the solvent polarity parameters $E_T(30)^{10}$ and Z¹³, which have been determined on absorption bands with intra- or intermolecular charge transfer character, respectively.

Contrary to betaines 3, compound 5 shows a bathochromic shift of its longest-wavelength absorption maximum as the solvent polarity is increased. This points to its ground state being less polar than the exited state, the latter one being more stabilized in polar solvents and, by hydrogen-bonding, hydroxylic solvents. In contrast to 5, the chemically but obviously not structurally related pyridinium betaine 7 displays a marked negative solvatochromism.¹⁴

EXPERIMENTAL

IR spectra: Perkin-Elmer 397 infrared spectrophotometer. All spectra were taken from KBr pellets. ¹H-NMR spectra: Varian EM-390 (90 MHz); TMS as internal standard. UV spectra: GCA:McPherson instrument. 1-cm quartz cells were used. Elemental analyses: Perkin-Elmer 240 Elemental Analyzer.

All solvents had been dried and kept over molecular sieves. Reaction steps, in which <u>la</u> or <u>lb</u> were involved, were carried out in a nitrogen or argon atmosphere. The following compounds were prepared according to published procedures: 9,9'-Oxy-bis(10-methylacridinium) bis(trifluorome-thanesulfonate) (<u>la</u>);¹⁵ 10-methyl-9-(trifluoromethanesulfonyl)oxy-acridinium trifluoromethanesulfonate (<u>lb</u>);¹⁵ 2,4-dioxo-1,8-trimethylene-1,2,3,4-tetrahydroquinoline;¹⁶ 3-hydroxyphenalene-1-one.¹⁷

General procedure for betaines 3a-h

The solution of 2.10 g (3 mmol) of <u>la</u> in 20 mL of acetonitrile was added dropwise to a mixture of 3 mmol of methylene compound (<u>2a-h</u>) and 2.15 g (6 m-equiv) of dimethylaminomethyl-polystyrene in 30 mL of acetonitrile. After stirring for an additional hour, the solvent was removed and the remaining solid was subjected to Soxhlet extraction with methanol until the extract was no longer colored. The solution was concentrated, and the two products (betaine <u>3</u> and 10-methyl-9(10H)acridinone <u>4</u>) were separated by column chromatography on silica gel (100 g) with methanol (300 mL). After stripping off the solvent, 50 mL of aqueous NaOH (0.1 N) were added, and the mixture was extracted repeatedly with chloroform until the color of the extract faded. The combined organic phases were concentrated and the precipitation of <u>3</u> was completed by addition of ether. All betaines were dried at 180 °C/0.003 Torr, but even under these conditions, not all water could be removed from most compounds.

5,5-Dimethyl-3-oxo-2-(10-methyl-9-acridinio)cyclohexene-1-olate (3a)

Black-green powder; 0.78 g (78 %); mp 284 $^{\circ}$ C (recrystallized from acetonitrile-ether); IR 3420, 2970, 2935, 1641, 1624, 1591, 1561, 1532, 1478, 1432, 1410, 1366, 1347, 1313, 1289, 1218, 1197, 1171, 1072, 1046, 1031, 1011 cm⁻¹; NMR (CD₃CN) δ 1.18 (s, 6H, C-CH₃), 2.38 (s, 4H, CH₂), 4.51 (s, 3H, N-CH₃), 7.59-7.82 (m, 2H), 8.05-8.46 (m, 6H). Anal. Calcd. for $C_{22}H_{21}NO_{2}$ ° 0.25 H₂0: C, 78.66; H, 6.45; N, 4.17; Found: C, 79.2; H, 6.51; N, 4.2.

The compound was also prepared from 1.47 g (3 mmol) of <u>lb</u>, but otherwise as described in the general procedure. Workup was as follows: After stirring for one additional hour, the mixture was filtered with suction, and the filtrate was concentrated to half the volume. Upon addition of ether, a black-green solid separated which was collected by filtration and to which was then added aqueous NaOH (0.1 N, 20 mL). Repeated extraction with chloroform gave 0.76 g (76 %) of 3a, which was identical with the product described above according to mp and spectral data.

1,3-Dimethyl-2,4-dioxo-5-(10-methyl-9-acridinio)-1,2,3,4-tetrahydropyrimidine-6-olate (3b)

Red-brown powder; 0.61 g (58 %); mp 343 $^{\circ}$ C; IR 3430, 1688, 1623, 1608, 1550, 1466, 1428, 1392, 1360, 1282, 1240, 1195, 1060, 1033 cm⁻¹; NMR (CDC1₃) δ 3.43 (s, 6H, N-CH₃), 4.49 (s, 3H, N⁺-CH₃), 7.49-7.79 (m, 2H), 7.90-8.10 (m, 4H), 8.48-8.79 (m, 2H). Anal. Calcd. for $C_{20}H_{17}N_{3}O_{3} = 0.25 H_{2}O$: C, 68.27; H, 5.01; N, 11.94. Found: C, 68.4; H, 5.01; N, 11.9.

2-(10-Methyl-9-acridinio)-3-oxo-phenalene-1-olate (3c)

Black-green powder; 0.85 g (73 %); mp 329 $^{\circ}$ C; IR 3430, 1639, 1622, 1589, 1559, 1539, 1526, 1498, 1470, 1448, 1428, 1397, 1348, 1300, 1280, 1240, 1201, 1184, 1160, 1120, 1082, 1039 cm⁻¹; NMR [(CD₃)₂S0] 5 4.82 (s, 3H, N-CH₃), 7.54-7.94 (m, 4H), 8.11-8.82 (m, 10 H). Anal. Calcd. for $C_{27}H_{17}NO_2$ · 0.25 H_2O ; C, 82.74; H, 4.50; N, 3.57. Found: C, 82.9; H, 4.47; N, 3.4.

6-Methyl-3-(10-methyl-9-acridinio)-6-oxo-2H-pyran-4-olate (3d)

Carmine powder; 0.79 g (82 %); mp 277 $^{\circ}$ C; IR 1666, 1641, 1622, 1588, 1546, 1521, 1511, 1461, 1438, 1411, 1396, 1379, 1330, 1300, 1277, 1201, 1168, 1127, 1051, 1038, 1000 cm⁻¹; NMR (CD₃OD) δ 2.32 (s, 3H, CH₃), 4.74 (s, 3H, N-CH₃), 5.97 (s, 1H), 7.63-7.91 (m, 2H), 8.08-8.32 (m, 2H), 8.38-8.62 (m, 4H). Anal. Calcd. for C₂₀H₁₅NO₃ $^{\circ}$ 0.25 H₂O: C, 74.64; H, 4.85; N, 4.35. Found: C, 74.8; H, 4.72; N, 4.4.

3-(10-Methyl-9-acridinio)-coumarin-4-olate (3e)

Red-brown powder; 0.92 g (87 %); mp 349 $^{\circ}$ C; IR 3440, 1662, 1613, 1586, 1552, 1530, 1474, 1438, 1401, 1320, 1272, 1229, 1204, 1182, 1118, 1071, 1042 cm⁻¹; NMR [(CD₃)₂SO] & 4.80 (s, 3H), 7.18 - 8.97 (m, 12H). Anal. Calcd. for C₂₃H₁₅NO₃ · 0.25 H₂O: C, 77.20; H, 4.36; N, 3.91. Found: C, 77.0; H, 4.42; N, 3.8.

1-Methyl-3-(10-methyl-9-acridinio)-2(1H)-quinolone-4-olate (3f)

Black-green powder; 0.75 g (78 %); mp 297 $^{\circ}$ C; IR 1640, 1619, 1591, 1549, 1492, 1452, 1421, 1346, 1290, 1241, 1218, 1191, 1140, 1120, 1068, 1049 cm⁻¹; NMR [(CD₃)₂S0] & 3.54 (s, 3H, N-CH₃), 4.70 (s, 3H, N⁺-CH₃), 6.98-8.68 (m, 12H). Anal. Calcd. for C₂₄H₁₈N₂O₂: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.4; H, 5.00, N, 7.6.

3-(10-Methyl-9-acridinio)-1,8-trimethylene-2(IH)-quinolone-4-olate (3g)

Black-green powder; 0.85 g (73 %); mp 302 $^{\circ}$ C; IR 3400, 1612, 1598, 1573, 1548, 1521, 1489, 1429, 1403, 1348, 1322, 1280, 1197, 1151, 1041 cm⁻¹; NMR (CD₃OD) & 1.97-2.38 (m, 2H), 2.89-3.22 (m, 2H), 4.04-4.37 (m, 2H, N-CH₂), 4.82 (s, 3H, N-CH₃), 6.90-8.80 (m, 11H). Anal. Calcd. for $C_{26}H_{20}N_2O_2$ $^{\circ}$ 0.25 H₂O: C, 78.67; H, 5.20; N, 7.06. Found: C, 78.4; H, 5.16; N, 7.0.

3-(10-Methyl-9-acridinio)-1,4-naphthoquinone-2-olate (3h)

Carmine powder; 0.42 g (38 %); mp 321 $^{\circ}$ C; IR 3450, 1692, 1621, 1600, 1548, 1432, 1370, 1310, 1289, 1231, 1204, 992 cm⁻¹; NMR (CD₃OD) & 4.83 (s, 3H, N-CH₃), 7.33-8.82 (m, 12H). Anal. Calcd. for $C_{24}H_{15}NO_3$ $^{\circ}$ 0.5 H_2O : C, 77.01; H, 4.30; N, 3.74. Found: C, 77.0; H, 4.15; N, 3.7.

9-Dibenzoylmethylene-10-methylacridan (5)

- a) From <u>la</u>: To a mixture of 0.67 g (3 mmol) of dibenzoylmethane and 2.15 g (6 m-equiv) of dimethylaminomethyl-polystyrene in acetonitrile (30 mL) was added a solution of <u>la</u> (2.10 g, 3 mmol) in acetonitrile (20 mL). After stirring for 2 h, the solvent was removed and the oily residue was chromatographed on a silica gel column (100 g) with ether-chloroform (4 : l v/v). This gave 0.30 g of unreacted dibenzoylmethyne, 0.30 g of 10-methyl-9(10H)-acridinone (4) and 0.40 g (0.96 mmol) of <u>5</u>. Data of <u>5</u>: Yellow powder (from ethyl acetate); mp 172 °C; IR 3070, 1662, 1616, 1502, 1482, 1372, 1321, 1260, 1190, 1159, 1132, 1004 cm⁻¹; NMR (CD₃CN) & 3.63 (s, 3H, N-CH₃), 6.63-6.88 (m, 2H), 7.11-7.62 (m, 12H), 7.83-8.05 (m, 4H). Anal. Calcd. for C₂₉H₂₁NO₂: C, 83.83; H, 5.09; N, 3.37. Found: C, 83.7 H, 5.26; N, 3.2.
- b) From 1b: The procedure was like in a), but with 1.47 g (3 mmol) of 1b instead of 1a. After column chromatography, one obtained 0.28 g of unreacted dibenzoylmethane, 0.06 g of 4 and 0.46 g (1.11 mmol) of 5.

<u>9-(5,5-Dimethyl-1-hydroxy-3-oxo-1-cyclohexene-2-yl)-10-methylacridinium trifluoromethane-</u> sulfonate (6)

Triflic acid (0.15 mL, 1.7 mmol) was added to the dark-green solution of 0.34 g (1 mmol) of 3a in 20 mL of acetonitrile. A yellow color appeared immediately. After concentrating to about 10 mL, 6 was precipitated as a yellow powder (0.47 g, 98%); mp 257 °C (from dichloromethane); IR 2660 br, 1650 vs, 1620 w, 1590 m, 1557 m, 1476, 1460, 1428 (all w), 1395 s, 1307 vs, 1250 vs, 1208 w, 1173 vs, 1102 w, 1040 vs cm⁻¹; NMR (CD₃CN) δ 1.34 (s, 6H), 2.80 (s, 4H), 4.67 (s, N-CH₃), 7.63 - 8.64 (m, 8H, Anal. Calcd. for C₂₃H₂₂F₃NO₅S: C, 57.37; H, 4.61; N, 2.91. Found: C, 57.0; H, 4.64; N, 2.8.

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