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CHARACTERIZATION OF SELECTED TRI-ARYLMETHANE LEUCONITRILES

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FOREWORD

The triarylmethane leuconitriles are of considerable interest in the field of eye protection, and information on their fundamental characteristics is not available. These data from spectroscopic studies of these compounds provide a basis for measurement of their basic photochemical properties.

The work was carried out in the Flame and Thermal Protection Section of the Chemical Modification of Textiles Branch of the Textile Research and Engineering Division under Materials for Flashblindness Protection, Project 1T062105A349, Task 05.

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I. INTRODUCTION

The use of photochromic compounds in optical (eye protective) devices has been under consideration for some time. (1,2,3,4) Construction of such a device, utilizing solutions of spiropyrans in filter cells surrounded by flash-tubes, has demonstrated the feasibility of this approach. The development of an optical device with satisfactory fundamental, bulk, and weight characteristics would require a significant improvement in speed of response, optical density, and non-fatiguing (recycling) properties.

As a class, the triphenylmethanes exhibit a higher extinction co-efficient and permit greater control of return rate than the spiropyrans.(7) The colorless leucocyanides of the triarylmethanes are converted by intense light to the highly-absorbing colored form. To furnish information essential to the development of a useable eye protective system, the characteristics of a series of systematically substituted triarylmethanes were measured.

Although some melting points and electronic spectra have been published for several of the leuconitriles of interest, a complete study of the properties of a series of these compounds was needed to permit elucidation of the mechanisms of color change and fatigue, and thereby provide a basis for improving the photochromic response and reducing side reactions.

II. OBJECTIVE

The objective of the present phase of the work with triarylmethanes was to synthesize and characterize completely (using uv, ir, nmr and mass spectral techniques) the leucocyanides of six triarylmethane dyes and one related model compound, triphenylacetonitrile.

III. DISCUSSION

Of the six di- and triamino substituted triarylmethane dyes needed for synthesis of the series of leucocyanides (1a through 3b), all but one were available.

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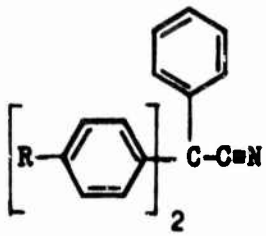

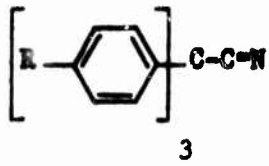

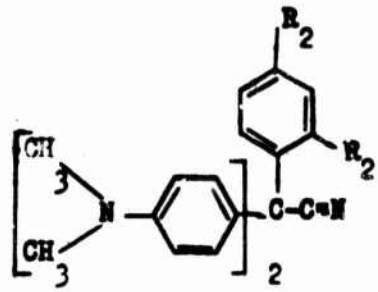

1a, R = NH_2 2a, R = NH_2 3a, R_1 = Cl, R_2 = H

1b, R = $N(CH_3)_2$ 2b, R = $N(CH_3)_2$ 3b, R_1 = CH_3, R_2 = NO_2

For Doebner's Violet (4,4'- diaminotriphenylmethyl cation), it was necessary to devise a satisfactory synthetic path. (The procedure described in the literature gave extremely poor yields; it is probable that none of the pure product was actually isolated). Neither the leuconitriles of Doebner's Violet (1a) nor of Turquoise Blue (3b) had previously been reported.

The general procedure followed for the synthesis of all the leuconitriles is given here in detail (4c) along with a tabulation of the specific conditions found best for each dye (Table I).

The complete characterization of the six leuconitriles was carried out. The resulting data, obtained by ir, nmr, uv, and mass spectral techniques, are given in Tables II and III. For those melting points and uv spectral characteristics which have been previously published, references to the original data are given.

IV. EXPERIMENTAL SECTION

A. Materials and Instrumentation

All melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. Ir spectra were determined in potassium bromide on a Perkin-Elmer Model 521 spectrometer. Nmr spectra were recorded

on either a Varian A-60 or HA-100 spectrometer with an internal tetramethylsilane standard. All the ultraviolet spectra were measured on a Cary 17 spectrometer in spectral grade solvents as indicated. A Perkin-Elmer Model 270 or a Consolidated Model 21-110 mass spectrometer was used. Elemental micro-analyses were performed by Midwest MicroLab, Ltd.

The following reagent grade dyes were used in the preparation of the leuconitriles: Crystal Violet, Pararosaniline Base (J. T. Baker Chemical Co.), Malachite Green (Matheson Co.), Turquoise Blue G (Verona Dyestuffs), and Brilliant Blue or Rhoduline Blue (GAF Corp.).

B. Preparation of Doebner's Violet Leuconitrile

1. 4,4' - Diaminotriphenylmethane[4]

The procedure of Baeyer and Villiger [8] was followed. In a 1-l three necked flask equipped with a condenser, mechanical stirrer, and glass stopper, were placed 76 ml (80 g, 0.76 mol) of benzaldehyde, 80 g (0.62 mol) of aniline hydrochloride, and 313 ml (320 g, 3.44 mol) of aniline. The solution was heated with stirring until it began to reflux (1 hr.). At this point the solution was allowed to cool. It was then made basic by the addition of 50 ml of a 60% sodium hydroxide solution. The resulting mass was extracted three times with 200 ml portions of hot acetone. The acetone solution was evaporated to a smaller volume (ca. 150 ml) and 150 ml of benzene was added. This solution was heated, decolorized with charcoal, filtered and dried over magnesium sulfate. Upon further reduction in volume, a solution was obtained which produced crystals when cooled.

A solution in benzene (120 ml/g) of the solid product was reduced to one half its original volume, yielding 4 (154.7 g, 0.564 mol, 74%): mp 107-09° (lit. [8] mp 105-06°) after four recrystallizations from benzene: ir 3440, 3360(N-H), 3060, 3020 (unsat. C-H), 2920. 2860, (aliphatic C-H). 1280 (C-N), 820 (p-aromatic), 750 and 700 cm^{-1} (monoaromatic), nmr ($COCL_3$), 87.16 (s,5), 6.88 (m,8), 5.32 (s,1,CH) and 3.41 ppm (s,2,NH_2).

The diacetate of 4,4' - diaminotriphenylmethane [5] was prepared in essentially 100% yield by treatment of 4 (150 g, 0.577 mol) with 150 ml (162 g, 159 mol) of acetic anhydride in 50 ml of glacial acetic acid (EXOTHERMIC). After one-half hour, the solvent was removed in a rotary evaporator. The product crystallized from methanol to give the desired product: mp 236-37° (Lit. [8] mp 233-35°): ir 3300, 3190, 3120 3050 (broad), 2920,2860, 1665, 1600, 1550, 1320, 810, 740, 720, and 700 cm^{-1}.

2. Attempted Oxidative Syntheses of Doebner's Violet

a. Oxidation with Manganese Dioxide

The reaction was carried out in a 300-ml Erlenmeyer flask with magnetic stirring. To a mixture of 5 g (0.014 mol) of 5 in 60 ml acetic acid, 9 ml sulfuric acid and 17 ml of water, 0.610 g (0.007 mol) of manganese dioxide (in another run, twice this amount of dioxide was used) were added with stirring and cooling in a water bath. The mixture was stirred vigorously for 36 hr and then treated with 25 g (0.5 mol) of potassium hydroxide in 25 ml of water. The material isolated after washing was unchanged starting material (~4.9 g; mp 236-37°).

b. Oxidation with Potassium Permanganate

To a solution of 5 in acid solution, as above, 0.865 g (0.0055 mol) of potassium permanganate in 20 ml of water were added at such a rate that the solution temperature was kept at ca. 10°. The solution was stirred for 15 additional minutes, 5 ml of ethanol added and finally 20 g (0.5 mol) of sodium hydroxide. The precipitate which formed was filtered and washed. It was identified as starting material (4.3 g; correct ir and mp).

This reaction was also attempted with three times the calculated amount of permanganate. In this run, the reaction mixture was slowly heated to reflux temperature. Again, only starting material could be recovered.

c. Oxidation with N-Bromosuccinimide (NBS)[9]

(1) Attempted Oxidation of Diacetyl-4,4'-diaminotriphenylmethane (5)

Compound 5 (5.0 g, 0.014 mol), 1.8 g (0.0101 mol) of NBS and 40 ml of carbon tetrachloride were mixed in a 100 ml round bottom flask equipped with reflux condenser. The mixture was refluxed in an oil bath for 32 hr. The starting material was recovered unchanged.

(2) Attempted Oxidation of Diacetyl-4,4'-diaminotriphenylmethane (4)

Compound 4 was treated in the manner described above for compound 5. The solvent was removed by evaporation, leaving a reddish tar. Infrared analysis showed the tar to contain a mixture of the reactants; none of the desired product could be identified.

(3) Attempted Oxidation of 4,4' - Diaminotriphenylmethane Catalyzed by Irradiation

In a [illegible] ml round bottom flask the di-p-animotriphenylmethane (3.0 g, 0.011 mol) and NBS (1.8 g, 0.0101 mol) in chloroform (50 ml) were refluxed for 6 hr under a 100-watt xenon mercury source. The small amount of precipitate which formed and remained after washing (3X) with carbon tetrachloride was composed (tlc on silica) mainly of NBS, probably some DV (small purple spot), a trace of 4, and unidentified resinous materials.

(4) Attempted Oxidation of 4,4' - Diaminotriphenylmethane Catalyzed by Irradiation and Benzoyl Peroxide

The triphenylmethane 4 was treated in chloroform solutions as above with 0.3 g (0.00123 mol, 10 mol %) benzoyl peroxide and NBS at reflux under irradiation for 28 hr. An additional 10 mol % of benzoyl peroxide was added and reflux continued for two more hr. The solvent was removed by evaporation and the solid remaining analyzed by tlc. Only trace amounts of the desired product could be detected.

3. 4,4'-Diaminotriphenylmethane

In a 100-ml reaction kettle equipped with an air condenser, 5.0g (0.018 mol) of 4,4'-diaminotriphenylmethanol (4), 4.50 g (0.0184 mol) of chloranil and 40 ml of chlorobenzene were heated with magnetic stirring at ca. 67°. After five hours the solution was allowed to cool and the insoluble products were separated by suction filtration. This crude product (5.52 g) was finely ground with a mortar and pestle, then extracted continuously with benzene in a Soxhlet extractor (48 hr) until essentially one spot was found with the tlc on silica gel (developed with 10% methanol in methylene chloride). This product was chromatographed on a silicic acid column (100 mesh). Elution with chloroform yielded tetrachlorohydroquinone (0.342 g, mp 233-35°C); with ether and 5% methanol in methylene chloride, untractable oils (successively yellow and green); and with increasingly polar 10-20% methanol in methylene chloride, Doebner's Violet, (3.45 g, 65.5%). The last material was a green powder which did not melt at temperatures below 350°C; however, it appeared to be a single compound from the tlc on silica gel: ir (KBr) 3400, 3290 (N-H), 3120, 1630, 1610, 1580, 1440, 1270, 1335, 1160, 895, and 620 cm^{-1}; nmr (DMSO-d_6) 8.40 (broad s, 2, NH_2), 7.06 (m, 13, aromatic), 3.48 ppm (broad s, 2, NH_2). Upon deuterium exchange the peaks at 8.40 and 3.49 ppm attributable to the ammonium and amino groups, respectively disappeared leaving the aromatic multiplet essentially unchanged.

To obtain very pure dye the material was chromatographed in the above manner twice. This insured the high purity (by tlc) of the dye which was necessary for the success of the conversion to leuconitrile.

4. The Leuconitrile of Doebner's Violet (1a)

A solution of 5.82 g (2.00 mmol) of Doebner's Violet (6) in 150 ml of methanol was heated on a steam bath and treated with 2.0 g (4.08 mmol) of sodium cyanide to produce a green colored mixture. The mixture was suction filtered, the filtrate evaporated to dryness on a rotary evaporator, and the residue extracted repeatedly (5X with 60 ml portions) with hot benzene. The benzene was decolorized with charcoal and reduced in volume to 100 ml to give crystals. These, upon recrystallization from benzene and ethanol containing a trace of sodium cyanide, gave 1a (4.35 g, 1.45 mmol, 72.5%): mp 225-26°; ir, 3480, 3390 (N-H), 3060, 2240 (C ≡ N), 1630, 1610, 1530, 1447, 1435, 1300, 1185, 830, 766, 705 cm^{-1}; nmr (DMSO-d_6) δ 7.2 (m, 5, aromatic), 6.65 (quartet, 8, aromatic), 5.22 and 4189 ppm (2, NH_2); mass spectrum (70 eV) m/e (relative intensity) 299 (71.9, M+), 223 (30.5), 222 (100), 207 (29.8), 195 (12.0), 190 (10.3), 182 (3.2), 150 (120), 28 (68.5).

C. General Procedure for Leuconitrile Preparation

The dye (~5g) was dissolved in a minimum amount of dimethylsulfoxide (shown in Table I) at ca. 85°. To this highly colored solution sodium cyanide (HOOD!) was added in small portions until the color of the dye was discharged. Charcoal was stirred into the hot solution. The mixture was filtered, the filtrate was heated to ca. 90°, and water was carefully added (See Table I) until the solution began to fog. The material forced out of solution was resolubilized by heating up to ca. 115°. The solution was allowed to slowly cool to 0° in order to produce crystals. The crystals were purified by repeated crystallization from solvents containing a trace of sodium cyanide. Table I gives the specific conditions and quantities used in the preparation of the various leuconitriles (1b, 2a-b, and 3a-b).

V. SUMMARY

While many triarylmethanes have been prepared, the yields of these preparations have often been poor. The present work describes a general procedure for producing these compounds with excellent yields even from relatively impure starting materials. The utility of the technique is demonstrated by the synthesis of several leuconitriles.

The comprehensive characterization of these compounds by spectral techniques gives largely new data which supports the proposed structures, and provides a basis for a study of the chemistry of this class of compounds.

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TABLE I

DETAILS OF PREPARATIVE PROCEDURES FOR LEUCONITRILES

Dye (g, mmol)	DMSO (ml, temp)	NaCN (g, moles)	Water (ml) Added	Recrystallization Solvent (ml/g)	Yield
Doebner's Violet[a] 1a (1 g, 3.5 mmol)	11 ml @ 80°	0.45 g, 9.2 mmol	10[c]	Benzene (22) Ethanol (--)	60%
Malachite Green 1b (10 g, 27.4 mmol)	300 ml @ 85°	4 g, 81.7 mmol	70	1:1 methanol ethylacetate (50)	62%
Pararosaniline, 2a (6.5 g, 23.6 mmol)	75 ml @ 85°	2 g, 40.8 mmol	160	95% ethanol (80)	49%
Crystal Violet 2b (7.5 g, 19.3 mmol)	80 ml @ 90°[b]	2.5 g, 50.9 mmol	10	Benzene (90)	68%
Brilliant Blue 3a (10 g, 25.6 mmol)	150 ml @ 85°	2.2 g, 44.8 mmol	50	1-propanol (40)	85°
Turquoise Blue 3b (10 g, 23.6 mmol)	225 ml @ 85°	2.5 g, 50.9 mmol	60	trace of ethylacetate 95% ethanol (80)	9%

a. An alternative technique with methanol as the solvent is described above (4b(4)).

b. After the initial filtration, hot benzene (ca. 200ml) removed most of the product (4.2 g) from the residue.

c. The leuconitrile could be isolated only upon vacuum distillation of the solvent.

TABLE II

PHYSICAL PROPERTIES OF TRIPHENYLMETHANE DERIVATIVES

Compound		Mp, °C	M[a]	ir, cm^{-1}		Nmr,	(ppm)
				3480, 3390	(N-H)	7.26	(s, 5, aromatic),
1a	$C_{20}H_{17}N_3$	226-27	299	2240	(C≡N)	6.65	(m, 8, aromatic),
				830	(para sub)		
				776, 705	(mono sub)	5.22,	4.89 (4,s,NH_2)[b]
				2920	(Aliph C-H)		(DMSO-d_6)
1b	$C_{24}H_{25}N_3$ (white crystals)	176-77 (Lit. (15) 176-77, (16) 188-89, (11) 173.7-74.5)	355	2230	(C≡N)	7.28	(2,5),
				812	para sub	6.86	(quartet,8),
				760, 700	mono sub	2.[illegible]3	(s,6,N-CH_3)
2a	$C_{20}H_{18}N_4$	207-08	314	3420, 3345	(N-H)	6.58	(quartet,12),
				2240	(C≡N)	5.34	(s,1),
				1280	(C-N)	4.82	(s,5) (DMSO-d_6)
				830	(para sub)		

TABLE II (Continued)

PHYSICAL PROPERTIES OF TRIPHENYLMETHANE DERIVATIVES

Compound		Mp, °C	M[a]	ir, cm^{-1}		Nmr,	(ppm)
2b	$C_{26}H_{30}N_4$ (white crystals)	293 (Lit.[11] 294-295.6)	398	2890, 2805	(alphi C-H)		
				2240	(C≡N)	6.85	(quartet,12),
				1230	(C-N)	2.92	(s,18,N-CH_3) ($CDCl_3$)
				815	(para sub)		
				2880, 2800	(aliphatic C-H)		
3a	$C_{24}H_{24}N_3Cl$ (brown crystals)	200.5	390	2230	(C≡N)	7.40	(m,2,aromatic),
				815	(para sub)	6.80	(quartet,10, aromatic),
				760, 767	(ortho sub?)	2.40	(s,12,N-CH_3) (DMSO-d_6)
3b	$C_{25}H_{26}N_4O_2$	197-201	414	2880, 2800	(aliph. C-N)	8.30	(m,1),
				2225	(C≡N)	7.59	(d,1),
				1355, 1340	(NO_2)	7.46	(d,1),
						6.85	(quartet,8),
				813	(para sub)	2.96	(s,12,NCH_3)
						2.39	(s,3) ($CDCl_3$)

TABLE II (Continued)

PHYSICAL PROPERTIES OF TRIPHENYLMETHANE DERIVATIVES

Compound		Mp, °C	M^a	ir, cm^{-1}		Nmr,	(ppm)
4	$C_{20}H_{15}N$	124.5-25.5 (Lit.[16] 124-25)	269	3060, 3030	(aromatic C-H)		
				2235	(C≡N)	7.26	(s)($CDCl_3$)
				750, 755, 765, 698	mono sub		

a. By mass spectroscopy (APPENDIX)
b. Deuterium exchange eliminated these absorption peaks to give further confirmation of their identity

TABLE III

U V SPECTRA[a]

Leuconitrile	B-Band (Max)	B-Band Max (X10+3)	R-Band (Max)	R-Band (X10+3)	Solvent
Doebner's Violet (1a)	252	28.55	295	2.90	Alcohol
	244	19.14	293	3.34	Methylcyclohexane
Malachite Green (1b)	273	43.36	305	5.95	Alcohol[11,12,13]
	271	43.50	303	5.63	Methylcyclohexane
Pararosanil (2a)	247	28.71	287	8.48	Alcohol[12,14]
Crystal Violet (2b)	272	61.24	305	8.35	Alcohol[11,12]
	277	55.74	305	10.[illegible]	Benzene
Brilliant or Rhodulina Blue (3a)	272	35.73	308	4.83	Alcohol[11,12]
	271	40.04	307	5.58	Methylcyclohexane
Turquoise Blue (3b)	272	44.63	[illegible]	[illegible]	Alcohol
	271	45.97	---	---	Methylcyclohexane

a. Spectra recorded in methylcyclohexane and benzene have not been reported previously.

APPENDIX

MASS SPECTRAL DATA

APPENDIX

MASS SPECTRAL DATA FOR TRIARYLMETHYL LEUCONITRILES AND RELATED SUBSTANCES. (RELATIVE ABUNDANCES AS A PERCENTAGE OF THE BASE PEAK)

A, Aniline. B, Phenylacetonitrile. C, N,N-Dimethylaniline. D, Triphenylacetonitrile. E, Doebner's Violet Leuconitrile. F, Pararosaniline Leuconitrile. G, Malachite Green Leuconitrile. H, Crystal Violet Leuconitrile. I, Rhodulina Blue Leuconitrile. J, Turquoise Blue Leuconitrile.

M/e	A	B	C	D	E	F	G	H	I	J
25	0.45	0.88	0.12					0.47		
26	2.22	5.69	1.42	1.2		6.8	1.2	1.36	1.7	1.04
27	3.01	9.94	4.43	8.0	7.6	12.7	2.3	5.25	6.0	1.92
28	6.99	62.42	3.33	13.8	68.5	100.0	38.5	4.33	9.2	1.79
29	0.40	3.07	0.80			7.21		0.86		2.28
30	0.67	1.40	0.61					1.22		1.30
31	0.34	5.08	0.52			16.98	5.8	0.51		2.18
32		12.66				21.4	7.7	0.88		
36	0.50	0.88								
37	4.10	5.87	1.20							
38	7.44	9.86	2.95							
39	17.32	22.60				21.1	6.2	5.74		
40	6.04	4.82	1.25							
41	5.96	3.37	2.09							
42	1.66	1.45	10.19				13.4	17.0	8.7	9.79
43	.69	3.07	1.97							
44		1.84	3.73		29.4	23.8				
44.5	1.06	0.88								
45		2.80	0.90							
45.5	1.97	1.40								
46		1.49								
46.5	7.02									
47	0.51									
49	0.81	2.80	0.62							
50	4.10	16.21	7.33					3.68		
51	4.48	22.43	16.25	4.1			4.9	6.11		4.15
52	5.47	4.56	5.10					3.78		
53	1.77	1.50	1.21							
54	4.74									
55						10.9			4.2	
58.5		3.24								

M/e	A	B	C	D	E	F	G	H	I	J
60			2.19						5.4	
60.5			4.65							
61	1.81	4.38								
62	2.67	8.59								
63	4.77	17.17	3.70	3.1		14.3		3.83		
64	2.87	6.88	2.24							
65	18.40	8.32	3.49		10.0			3.01		
66	33.68	1.31	1.08							
67	4.62									
69					6.5					
74	1.10	3.94	2.05							
75	0.60	3.29	1.61					2.18		
76	1.25	2.76	1.68			8.0		5.04		
77	1.25	9.37	24.74	14.6	3.8		6.6	12.0	3.4	9.24
78	1.82	1.71	6.18				3.0	10.2		
79			4.37					4.30		
87	2.19	2.19								
88	3.94	3.94						2.30		
89		23.16								7.17
90	0.23	40.47	0.91			12.6		2.97		4.15
91	0.97	22.78	4.55			14.0		4.92		5.55
92	11.13	10.42	1.89		7.6	4.8		2.55		
93	100.00	0.96	1.26					1.76		
94	6.99		0.82		6.5					
95	0.21									
95.5										3.89
101								0.39		
102								0.41		
103			2.81					0.57		
104			10.94			8.0		1.54		8.73
105			12.81					1.82		
106			3.66					1.19		
108							5.4			
113				3.1	7.4			1.66		
114		0.57		2.5				2.26		
115		1.75		6.9				2.22		
116		37.58		2.2				2.78		
117		100.00	0.73					2.11	4.8	
118		9.95	3.27			30.3		5.36	5.8	7.47

M/e	A	B	C	D	E	F	G	H	I	J
119			2.13	2.5		6.1		9.31		14.6
119.5										6.69
120			100.00	2.2				6.25	7.5	13.3
121			69.47	1.6				2.75		4.95
122			5.77	3.1				0.63		
122.5								1.26		
123			0.23					1.02		
124										
125								1.10		
126				2.5				1.76		4.31
127				1.8				1.35		
128				1.3				1.22		
129								1.07		
130							6.3	1.29		3.45
130.5								5.19		16.3
131								1.76	7.3	7.48
131.5										3.68
132								0.84		2.67
132.5								1.32		
133								0.80		
133.5								0.30		
134								6.36		
134.5								1.21		
135								1.37		
135.5								0.56		
136								1.13		
137								0.42	14.2	
138					5.4			0.78	9.2	10.5
139								4.76	3.3	61.4
139.5								2.69		22.7
140				6.8						3.06
140.5								0.84		
141				4.3				1.11		
141.5								3.46		
142					6.5			3.13		
142.5						8.8		3.09		

M/e	A	B	C	D	E	F	G	H	I	J
143										
144								4.01		3.99
145								1.36		2.49
146								1.34		5.04
147							13.9	0.83		
148							5.4	0.77		
149								1.07		3.58
150				1.7				0.79		
151				2.2	12.0	7.1		0.87		2.52
152				6.4	3.7	6.1		2.08		3.83
153				3.6	9.4			2.64	3.3	4.48
154				2.2	4.3			2.09		4.27
155					7.4			1.69		
156					4.0			1.44		
157								0.99		
158								2.69		4.95
159								10.5		4.93
160								3.91		
161								1.56		
162								---		
163								0.73		3.10
164								2.30		6.14
165				15.3			2.7	2.24		4.65
166				2.52		12.2	9.5	3.61	3.8	7.36
167				100.0	3.9	10.5	2.7	1.15		3.34
168				38.0		4.9		0.65		
170								1.00		
170.5								1.03		
171					4.0			0.74		3.11
172								0.80		
175								0.63		
175.5							2.3	0.69		
176							7.2	0.77		
176.5							3.4	1.31		
177								2.44		3.01
17715								3.84	4.4	5.24
178				6.0	8.2			3.82		6.71
179								2.60		4.92
180						17.1		0.77		
								0.98		

M/e	A	B	C	D	E	F	G	H	I	J
181					13.1	5.4		0.76		3.45
182					13.2	6.05		0.72		
183						--		1.55		3.06
183.5										8.38
184						7.1		0.60		10.4
185						5.5		0.58		
185.5								3.00		
186								1.77		
187								0.58		
188								0.64		4.22
189								1.53		4.71
190					10.3		13.5	11.9	14.0	16.2
191				27.2			6.1	4.67	4.0	5.66
192				21.3				2.33		4.27
193				58.9				1.69		2.90
194				11.2				1.02		2.85
194.5									5.4	4.15
195					12.0	23.1		1.57	2.5	2.59
195.5									5.0	
196					2.2	31.4		1.35		
197					4.3	45.0		0.83		2.28
198						14.7		0.84		
199								5.87		
199.5								2.04		
200								0.43		
201				1.2				0.46		2.59
202				1.0				0.89		3.17
203				1.4				1.22		7.21
204				0.7				0.92		5.53
205					9.8			0.88		4.66
206					5.4			0.98		3.35
207					29.8			1.00		6.60
208					5.4		2.9	3.16		5.15
209							4.0	2.68	4.6	3.37
210							1.2	1.00		
211								0.68		
212						8.0		--		
213						19.4		0.41		
214				1.6		4.1		0.58		
215				1.2				0.59		

M/e	A	B	C	D	E	F	G	H	I	J
216										
217				2.2				0.64		3.14
218								1.66		4.30
219								1.83		4.93
220							5.2	2.88		6.16
221					6.5			1.42	4.7	6.15
222					3.6			1.28		6.16
223					100.00	5.0		0.89		3.90
224					30.5			1.39		2.67
225								2.37		2.52
226						4.6		3.40		2.62
227								0.34		2.74
228				1.7				0.58		2.54
229				1.3				0.77		2.00
230				1.3				0.39		1.58
231								0.42		1.68
232								0.42		2.80
233						4.8		1.23		5.25
234							5.5	5.87		13.8
235							3.2	3.98	7.2	6.12
236							19.1	2.76		4.64
237							3.8	1.13		1.56
238								2.54		3.39
239								0.96		
240				6.5				3.99		4.61
241				4.5				15.2		9.44
242				9.3				3.60	2.2	2.07
243				5.5		3.9		0.60		2.27
244				4.3		4.8		0.30		2.33
245				2.4				0.44		
246								0.36		2.85
247								2.12		4.80
248								1.90		7.42
249								1.77		5.67
250								0.60		2.74
251								0.48		2.85
252								0.92		2.33
253				1.3				5.57		2.49
254				1.6				27.6		5.17
								0.85	2.1	2.71

M/e	A	B	C	D	E	F	G	H	I	J
255				1.7				0.38		2.05
256				1.7				0.28		
257								0.28		
258								0.27		
259								0.22		
260								0.75		
261								0.50		34.1
262							13.4	18.8		9.64
263							3.2	4.63	9.8	11.0
264								2.21	4.7	3.90
265								0.70	9.8	2.25
266								0.39		7.25
267								0.36		2.67
268				27.2				0.73		5.88
269				93.7				0.43		
270				22.6					8.3	
271				12.7	2.7				2.5	
272					1.1				3.5	
273					1.1					
274					5.4					
275					6.0					2.94
276								1.39		2.46
277								1.05		100.00
278							100.00	100.00		30.6
279							16.7	20.9	100.00	4.95
280							2.3	2.82	27.3	2.02
281								0.41		2.02
282								0.28		1.56
283								0.23		1.81
284								0.35		
285								0.32		
286						4.3		0.24		
287						27.9				
288						45.7				
290						49.1				
291						19.4				5.00

M/e	A	B	C	D	E	F	G	H	I	J
292										2.46
293								0.36		4.68
294								0.29		2.66
295								0.41		
296								0.50	1.7	
297										
298					9.8					
299					72.9					
300					27.2					
301					2.2					
302										1.37
305						11.8				
306						8.5				
308										1.81
309								0.32		
310								0.37	2.1	
311						3.0	1.7	0.62	2.2	
312								0.58	2.4	
313							2.1	0.39		
314						6.1		0.71		
315						3.1				
316						3.9				
317										
318										
319						3.5				
324								0.47		
325								0.27		2.02
326								0.27		
327								0.36		
328								0.60		
329							3.5	0.25		
330							1.6	0.23		
338										
339								0.73		
340								0.35		
341								1.10		
342								0.85		
343								0.55		
346								0.23		
347									2.3	
348									1.4	1.74
349									2.5	
									1.3	

M/e	A	B	C	D	E	F	G	H	I	J
352								0.28		
353								0.41	1.5	
354							3.5	4.46	2.9	1.72
355							43.3	1.69	0.9	
356							13.3	2.62	0.8	
357							1.7	0.85	1.7	
358								0.43		
359								0.35		
363										1.35
364									4.0	
365									2.4	
366									2.4	
370										2.67
371								3.98		
372								1.62		1.92
373								0.50		
374										
375									2.1	1.56
376									3.2	
377										
378									1.7	
379									1.3	
380								0.38		
381								0.38		
382								0.70		
383								0.67		
384								0.14		3.84
388										3.45
389									2.5	14.5
390									53.4	4.27
391									16.7	5.39
392									21.9	1.92
393									7.9	
394									1.2	
395								0.48		
396								2.32		
397								28.3		
398								8.79		1.35
399								1.90		1.48
400								0.25		3.38
413										3.68
414										40.2
415										9.54
416										1.77