Mass Spectra of Substituted Pyrazolo[1,5-*a*]-1,3,5-triazines

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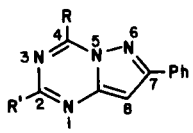
High resolution electron impact mass spectrometric measurements have been made on twelve pyrazolo[1,5-*a*]-1,3,5-triazines. Substituents attached to carbon atoms 2, 4, 7, and 8 were used to label the various fragments. Three major ions were observed (a) the molecular ion, (b) an ion corresponding to M-RCN where R is the substituent attached to C-4 and (c) an aryl cyclopropenyl cation which was observed in 7-aryl derivatives. Intensities and accurate mass-measurements are given for all ions having intensities exceeding 2% of the base peak. Nine of the twelve pyrazolo-[1,5-*a*]-1,3,5-triazines included in this study are described here for the first time.

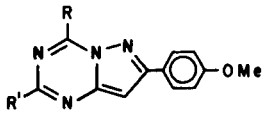
The mass spectra of numerous *s*-triazines have been studied to understand the fragmentation pattern of this important class of heterocycles (2-4) and to identify the metabolites of triazine herbicides (5). Mass spectrometry has revealed interesting fragmentation pathways including unusual transfer of hydrogen atoms from the side chain to ring nitrogens of *s*-triazines.

The work described in this paper deals with a high resolution mass spectrometric study of twelve substituted pyrazolo[1,5-*a*]-1,3,5-triazines (compounds **1-12**) which were chosen from a series of compounds synthesized for screening as c-AMP phosphodiesterase inhibitors (6-11), and in part described here. The various alkyl and aryl substituents attached to carbon atoms 2, 4, 7, and 8 of pyrazolo[1,5-*a*]-1,3,5-triazines were used as labels to help trace the origin of the various fragments in the mass spectra.

The compounds studied (see Table I) may be divided into four types (**Ia**, **Ib**, **Ic**, and **II**), according to the substituent attached to the pyrazole ring and its position of attachment. In type **Ia** (compound **1-7**) a phenyl group was attached to position 7 of the pyrazolo[1,5-*a*]-1,3,5-



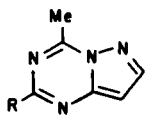
Ia



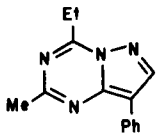
Ib

1; R = H , R' = Me
2; R = Me , R' = Me
3; R = Me , R' = Et
4; R = Et , R' = Me
5; R = n-Pr , R' = Me
6; R = Me , R' = Ph
7; R = Ph , R' = Me

8; R = Et , R' = Me
9; R = Et , R' = Et



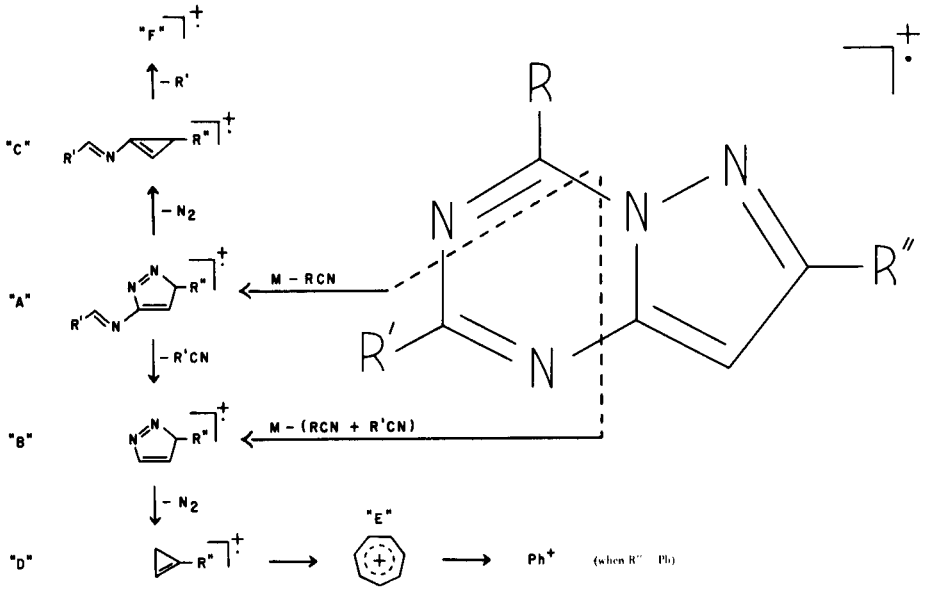
Ic



II

10; R = Me
11; R = Ph

12



Scheme I

triazine. In type **Ib** (compound **8,9**) the phenyl ring was replaced with a *p*-anisyl group in the same position, and in type **Ic** (compound **10,11**) the pyrazole ring was unsubstituted. In one example, designated **II** (compound **12**) a phenyl group was attached to position 8 of the pyrazolo[1,5-*a*]-1,3,5-triazine.

Compounds **Ia** were characterized by three major peaks, the molecular peak "$M^{+\cdot}$", a peak "A", corresponding to the loss of RCN, and the phenylcyclopropenyl cation "D" (see Scheme I). In view of the stability of the polyannular system, the molecular peak in most compounds has an intensity of more than 90%. However, in compounds **4**

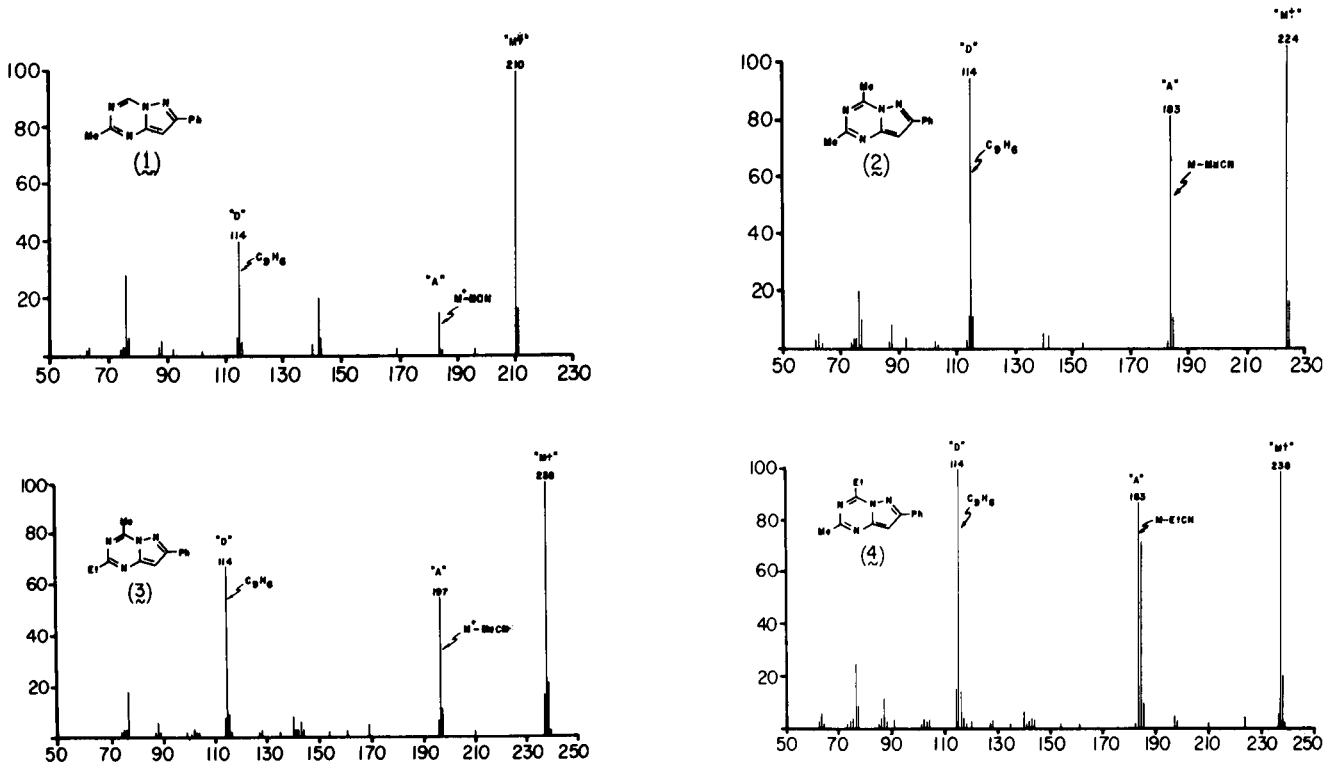


Figure 1. Mass Spectra of Compounds **1**, **2**. **3**, **4**.

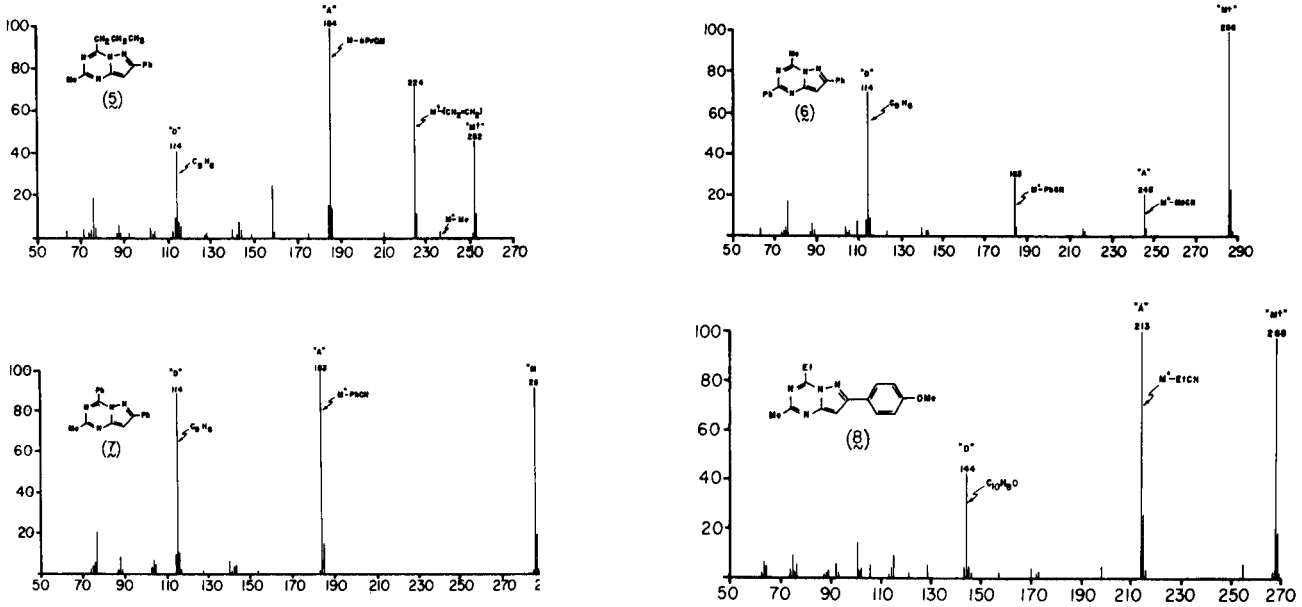


Figure 2. Mass Spectra of Compounds **5**, **6**, **7**, **8**.

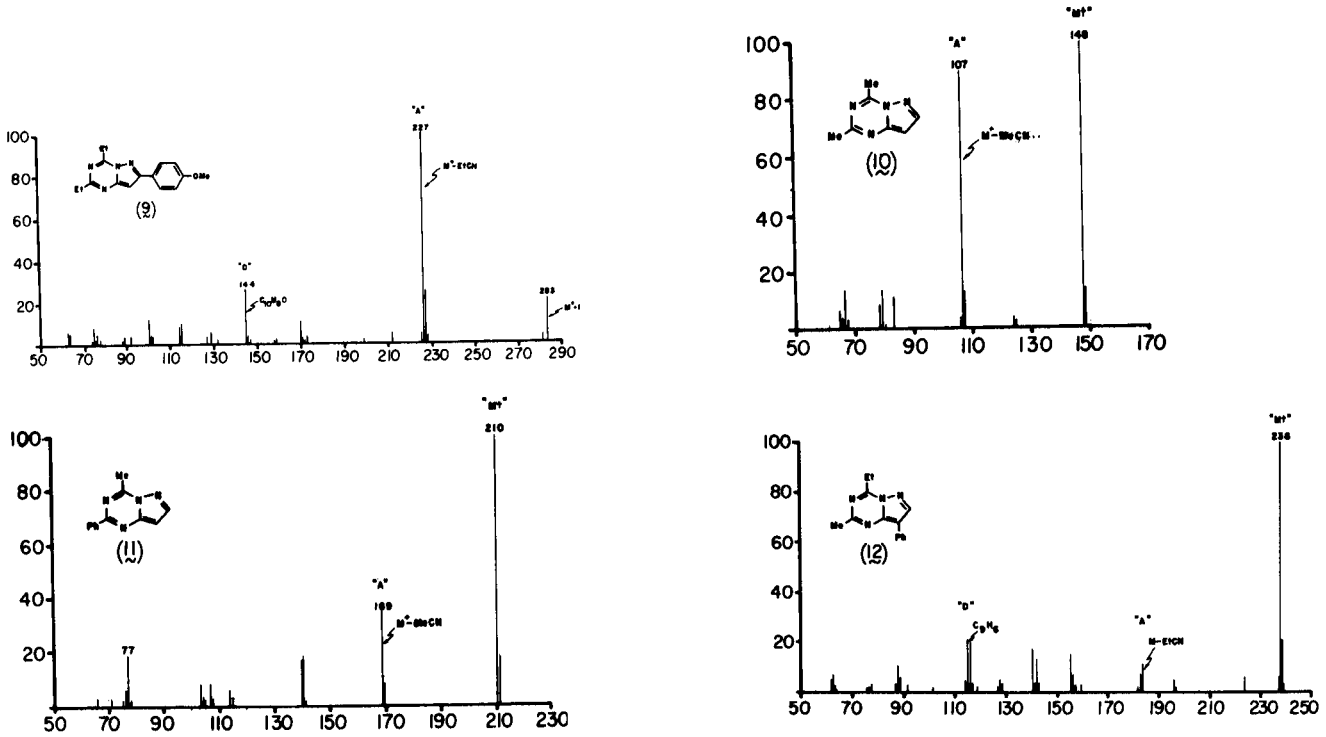
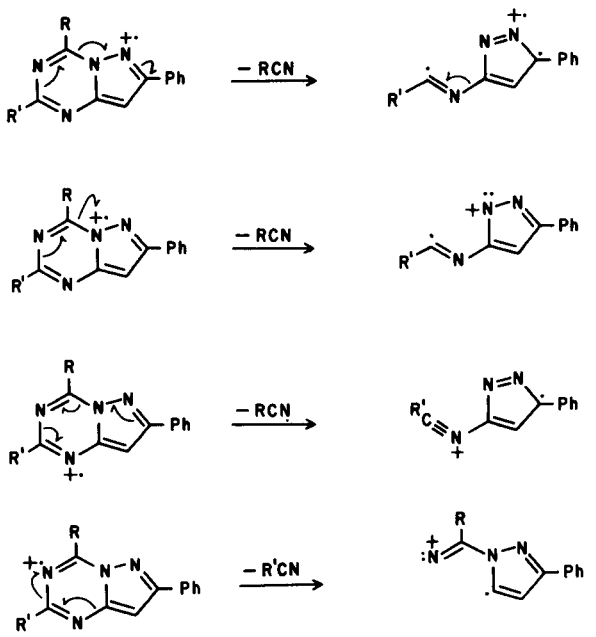


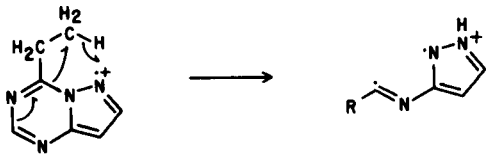
Figure 3. Mass Spectra of Compounds **9**, **10**, **11**, **12**.

and **5** (see Figure 1 and 2), which were substituted with *n*-propyl or ethyl groups in position 4 of the pyrazolo-[1,5-*a*]-1,3,5-triazines, weaker molecular peaks were observed because of the facile splitting of the alkyl chain.

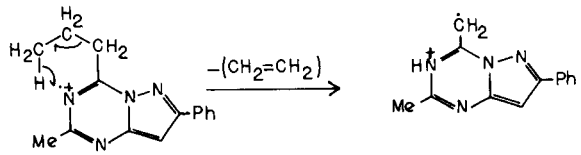
Another major peak in compounds **1a** was a peak equivalent to M-RCN which was designated "A". Because the triazine rings were substituted with different substituents it was possible to establish that it was the R substituent, attached to position 4 of the pyrazolo[1,5-*a*]-1,3,5-triazine and not R′, attached to position 2 that was eliminated during electron bombardment to give fragment "A". The loss of R′CN was usually of less than 2% intensity except when R′ was a phenyl group that stabilized the PhCN ion by resonance (see Figure 2 for the spectrum of compound **6**). The predominance of ion "A" (M-RCN) over the M-R′CN fragment was attributed to the fact that a positive charge on three of the four nitrogen atoms in pyrazolo[1,5-*a*]-1,3,5-triazines could lead to the ion radical "A" or an isomer of equal mass, whereas only a charge on the fourth nitrogen would give the fragment M-R′CN.



Ion "A" had relative intensities ranging from 100 to 15% and when the substituent R, attached to position 4 of the pyrazolo[1,5-*a*]-1,3,5-triazine, was an alkyl group larger than a methyl such as an ethyl or a propyl group, as for example in compounds **4** and **5**, a significant peak equivalent to AH (a protonated A) was observed. Similar protonations were observed by Preston and coworkers (2). The formation of such protonated fragments can be easily explained by a McLafferty type rearrangement that would protonate the nitrogen in the pyrazole ring.



In the case of the propyl substituted compound (**5**), a McLafferty rearrangement involving the nitrogen of the triazine can take place to give an M-(CH_2=CH_2) peak that is actually quite significant.



A usually weak ion (less than 5%) observed in the mass spectra of compounds **1a**, is a radical ion of mass equivalent to M-(RCN + R′CN) which was designated "B". This ion "B" can be formed from either the molecular ion "$M^{+\cdot}$" or from ion "A".

When ion "B" loses two nitrogen atoms, it is converted into a very stable or abundant ion "D" which corresponds to the Hückel aromatic phenyl-cyclopropenyl cation, which together with the molecular ion "$M^{+\cdot}$" and ion "A" represent the three major peaks in the spectra of compounds **1a**. Ion "D" is further split to give first a cycloheptenyl cation and then a phenyl ion.

In addition to giving ion "B", ion "A" can lose two nitrogen atoms and give a relatively low intensity ion "C" which in turn gives an ion "F" that corresponds to the loss of the substituent R′ originally attached to position 2 of the pyrazolo[1,5-*a*]-1,3,5-triazine. This ion "F" is quite weak and in only one case has a relative intensity above 2%.

The introduction of a *p*-anisyl group in position 7 of the pyrazolo[1,5-*a*]-1,3,5-triazine (compound **1b**) resulted in a decrease in the intensity of ions "B" and "E", and complicated the phenyl ring fragmentation by the usual (12) anisyl breakdown pattern (see Figure 2 and 3 for the spectra of compounds **8** and **9**).

A more dramatic change occured when the phenyl group was removed from the pyrazole ring (compounds **1c**). In this case ions "B", "C", "D", and "E" became either quite insignificant or totally absent and there was a great increase in the intensity of ion "F" (see Figure 3, for the spectra of compounds **10** and **11**).

Another change occured when the position of the phenyl group was changed from position 7 to position 8 of the pyrazolo[1,5-*a*]-1,3,5-triazine (compound **12**). In this case ion "A" became quite small and so did ions "B", "C", "D", and "E" (see Figure 3 for the spectrum of compound **12**).

The present study will be of use in differentiating the structures of isomeric pyrazolo[1,5-*a*]-1,3,5-triazines proposed in earlier work (9). Thus, the major fragment "A" (M-RCN) can help decide whether a group R is in position 2 or 4. Further, Scheme I might be of value in identifying the metabolites of these c-AMP phosphodiesterase inhi-

Table I

2-Methyl-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**1**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
211.0922	211.0939	16	$C_{11}{}^{13}CH_{10}N_4$	
210.0890	210.0905	100	$C_{12}H_{10}N_4$	$M^{+\cdot}$
183.0787	183.0796	14	$C_{11}H_9N_3$	M-RCN "A"
143.0577	143.0564	6	$C_8{}^{13}CH_6N_2$	
142.0514	142.0531	20	$C_9H_6N_2$	"B"
140.0491	140.0500	3	$C_{10}H_6N$	"F"
114.0458	114.0469	40	C_9H_6	"D"
113.0392	113.0391	6	C_9H_5	
91.5391	183.0787	2	$C_{11}H_9N_3$ (d. i)	
88.0302	88.0313	5	C_7H_4	"E"
78.0418	78.0425	3	$C_5{}^{13}CH_5$	
77.5374		4		
77.0383	77.0391	28	C_6H_5	Ph
76.0305	76.0313	2	C_6H_4	
68.0383	68.0374	2	$C_3H_4N_2$	
63.0319		2		

2,4-Dimethyl-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**2**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
225.1094	225.1095	17	$C_{12}{}^{13}CH_{12}N_4$	
224.1058	224.1062	100	$C_{13}H_{12}N_4$	$M^{+\cdot}$
184.0828	184.0830	12	$C_{10}{}^{13}CH_9N_3$	
183.0795	183.0796	78	$C_{11}H_9N_3$	M-RCN "A"
142.0523	142.0531	4	$C_9H_6N_2$	"B"
140.0492	140.0500	5	$C_{10}H_6N$	"F"
115.0493	115.0503	11	$C_8{}^{13}CH_6$	
114.4057	114.0469	92	C_9H_6	"D"
113.0392	113.0391	11	C_9H_5	
91.5401	183.0795	3	$C_{11}H_9N_3$ (d. i.)	
88.0314	88.0313	8	C_7H_4	"E"
87.0247	87.0235	2	C_7H_3	
78.0423	78.0425	2	$C_5{}^{13}CH_5$	
77.0397	77.0391	20	C_6H_5	Ph
76.0320	76.0313	2	C_6H_4	
75.0241	75.0235	3	C_6H_3	
63.0255	63.0235	4	C_5H_3	

2-Ethyl-4-methyl-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**3**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
239.1262	239.1252	21	$C_{13}{}^{13}CH_{14}N_4$	
238.1179	238.1218	100	$C_{14}H_{14}N_4$	$M^{+\cdot}$
237.1107	237.1140	17	$C_{14}H_{13}N_4$	M-1
198.0997	198.1031	11	$C_{12}H_{12}N_3$	
197.0958	197.0953	57	$C_{12}H_{11}N_3$	M-RCN "A"
196.0822		7		
169.0629	169.0640	5	$C_{10}H_7N_3$	
161.0803	161.0827	2	$C_8H_9N_4$	
144.0651		2		
143.0579		6		
142.0528	142.0531	3	$C_9H_6N_2$	"B"
141.0543	141.0534	3	$C_9{}^{13}CH_6N$	
140.0499	140.0500	9	$C_{10}H_6N$	"F"
115.0493	115.0503	9	$C_8{}^{13}CH_6$	
114.0452	114.0469	64	C_9H_6	"D"
113.0373	113.0391	8	C_9H_5	
102.0450	102.0469	3	C_8H_6	
88.0317	88.0313	6	C_7H_4	"E"
77.0383	77.0391	18	C_6H_5	Ph
76.0301	76.0313	2	C_6H_4	
75.0219	75.0235	2	C_6H_3	

4-Ethyl-2-methyl-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**4**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
239.1269	239.1252	20	$C_{13}{}^{13}CH_{14}N_4$	
238.1232	238.1218	99	$C_{14}H_{14}N_4$	$M^{+\cdot}$
237.1125	237.1140	5	$C_{14}H_{13}N_4$	M-1
224.1048	224.1062	3	$C_{13}H_{12}N_4$	
198.0999	198.1031	3	$C_{12}H_{12}N_3$	
197.0923	197.0953	4	$C_{12}H_{11}N_3$	M-R″CN
185.0896	185.0908	8	$C_{10}{}^{13}CH_{10}N_3$	
184.0850	184.0875	71	$C_{11}H_{10}N_3$	
183.0784	183.0796	86	$C_{11}H_9N_3$	M-RCN "A"
182.0692	182.0718	2	$C_{11}H_8N_3$	
154.0678	154.0657	2	$C_{11}H_8N$	
144.0680	144.0687	3	$C_9H_8N_2$	
143.0600	143.0609	4	$C_9H_7N_2$	
142.0539	142.0531	3	$C_9H_6N_2$	"B"
140.0487	140.0500	7	$C_{10}H_6N$	"F"

Table I (Continued)

4-Ethyl-2-methyl-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**4**) (Continued).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
128.0508	128.0500	3	C_9H_6N	
119.0613	119.0609	3	$C_7H_7N_2$	
115.0484	115.0503	14	$C_8{}^{13}CH_6$	
114.0448	114.0469	100	C_9H_6	"D"
113.0381	113.0391	15	C_9H_5	
104.0492	104.0500	3	C_7H_6N	
102.0450	102.0469	4	C_8H_6	
89.0372	89.0391	3	C_7H_5	"E"
88.0309	88.0313	11	C_7H_4	
87.0246	87.0235	4	C_7H_3	
78.0427	78.0425	4	$C_5{}^{13}CH_5$	
77.5376		5		
77.0382	77.0391	24	C_6H_5	Ph
76.0276		4		
75.0196		3		
74.0128		2		
63.0342		5		
62.0291		3		

2-Methyl-4-*n*-propyl-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**5**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
253.1405	253.1408	11	$C_{14}{}^{13}CH_{16}N_4$	
252.1368	252.1375	45	$C_{15}H_{16}N_4$	$M^{+\cdot}$
251.1275	251.1297	2	$C_{15}H_{15}N_4$	M-1
237.1122	237.1140	4	$C_{14}H_{13}N_4$	
225.1087	225.1095	11	$C_{12}{}^{13}CH_{12}N_4$	
224.1052	224.1062	72	$C_{13}H_{12}N_4$	M-(CH_2=CH_2)
223.0966	223.0984	2	$C_{13}H_{11}N_4$	
210.0955		2		
185.0897	185.0908	13	$C_{10}{}^{13}CH_{10}N_3$	
184.0852	184.0875	100	$C_{11}H_{10}N_3$	
183.0784	183.0796	15	$C_{11}H_9N_3$	"A"
175.0972	175.0984	2	$C_9H_{11}N_4$	
160.0819	160.0830	3	$C_8{}^{13}CH_9N_3$	
159.0792	159.0796	24	$C_9H_9N_3$	
142.0512	142.0531	2	$C_9H_6N_2$	"B"
140.0488	140.0500	3	$C_{10}H_6N$	"F"
128.0521	128.0500	2	C_9H_6N	
114.0464	114.0469	41	C_9H_6	"D"
113.0390	113.0391	9	C_9H_5	

2-Methyl-4-*n*-propyl-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**5**) (Continued).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
104.0496	104.0500	3	C_7H_6N	PhCNH
102.0465	102.0469	4	C_8H_6	
92.0456		2		
89.0390	89.0391	3	C_7H_5	
88.0322	88.0313	7	C_7H_4	"E"
87.0257	87.0235	2	C_7H_3	
77.5375		3		
77.0382	77.0391	19	C_6H_5	Ph
76.0309	76.0313	2	C_6H_4	
75.0223	75.0235	2	C_6H_3	
71.0481	71.0483	3	$C_2H_5N_3$	
63.0315		3		

4-Methyl-2,7-diphenylpyrazolo[1,5-*a*]-1,3,5-triazine (**6**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
287.1226	287.1252	23	$C_{17}{}^{13}CH_{14}N_4$	
286.1184	286.1218	100	$C_{18}H_{14}N_4$	$M^{+\cdot}$
246.0997	246.1031	4	$C_{16}H_{12}N_3$	
245.0967	245.0953	21	$C_{16}H_{11}N_3$	M-RCN "A"
217.0860	217.0891	2	$C_{16}H_{11}N$	F
216.0785	216.0813	4	$C_{16}H_{10}N$	F-1
184.0829	184.0830	4	$C_{10}{}^{13}CH_9N_3$	
183.0792	183.0796	29	$C_{11}H_9N_3$	M-PhCN
142.0519	142.0531	2	$C_9H_6N_2$	"B"
140.0509	140.0500	4	$C_{10}H_6N$	"F"
115.0491	115.0503	9	$C_8{}^{13}CH_6$	
114.0454	114.0469	70	C_9H_6	"D"
113.0387	113.0391	8	C_9H_5	
103.0432	103.0422	5	C_7H_5N	PhCN
89.0395	89.0391	2	C_7H_5	
88.0333	88.0313	7	C_7H_4	"E"
87.0254	87.0235	2	C_7H_3	
77.0374	77.0391	18	C_6H_5	Ph
76.0301	76.0313	3	C_6H_4	
75.0210	75.0235	2	C_6H_3	

Table I (Continued)

2-Methyl-4,7-diphenylpyrazolo[1,5-*a*]-1,3,5-triazine (**7**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
287.1243	287.1252	20	$C_{17}{}^{13}CH_{14}N_4$	
286.1221	286.1218	92	$C_{18}H_{14}N_4$	$M^{\ddagger}$
245.0938	245.0953	2	$C_{16}H_{11}N_3$	M-R′CN
224.1058	224.1062	2	$C_{13}H_{12}N_2$	
184.0824	184.0830	15	$C_{10}{}^{13}CH_9N_3$	
183.0784	183.0796	100	$C_{11}H_9N_3$	M-RCN "A"
143.0605	143.0609	4	$C_9H_7N_2$	
142.0522	142.0531	3	$C_9H_6N_2$	"B"
140.0486	140.0500	5	$C_{10}H_6N$	"F"
116.0492	116.0500	2	C_8H_6N	
115.0490	115.0503	10	$C_8{}^{13}CH_6$	
114.0460	114.0469	87	C_9H_6	
113.0391	113.0391	10	C_9H_5	
104.0498	104.0500	4	C_7H_6N	
103.0430	103.0422	6	C_7H_5N	PhCN
88.0318	88.0313	9	C_7H_4	"E"
87.0247	87.0235	2	C_7H_3	
78.0426	78.0425	2	$C_5{}^{13}CH_5$	
77.0387	77.0391	21	C_6H_5	
76.0315	76.0313	4	C_6H_4	
75.0230	75.0235	2	C_6H_3	
74.0156	74.0156	2	C_6H_2	
63.0341		2		

7-*p*-Anisyl-4-ethyl-2-methylpyrazolo[1,5-*a*]-1,3,5-triazine (**8**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
269.1359	269.1358	19	$C_{14}{}^{13}CH_{16}N_4O$	
268.1327	268.1324	99	$C_{15}H_{16}N_4O$	$M^{\ddagger}$
267.1252	267.1246	2	$C_{15}H_{15}N_4O$	M-1
254.1156	254.1168	5	$C_{14}H_{14}N_4O$	
215.0993	215.0969	3	$C_{10}{}^{13}C_2H_{11}N_3O$	
214.0960	214.0980	27	$C_{12}H_{12}N_3O$	
213.0907	213.0982	100	$C_{12}H_{11}N_3O$	M-RCN "A"
198.0676	198.0667	3	$C_{11}H_8N_3O$	
170.0606	170.0606	3	$C_{11}H_8NO$	"F"
146.0608	146.0629	2	$C_6{}^{13}C_2H_6N_3$	
145.0614	145.0595	5	$C_7{}^{13}CH_6N_3$	
144.0557	144.0575	42	$C_{10}H_8O$	"D"
143.0500	143.0497	4	$C_{10}H_7O$	
129.0355	129.0340	6	C_9H_5O	
115.0535	115.0548	9	C_9H_7	

7-*p*-Anisyl-4-ethyl-2-methylpyrazolo[1,5-*a*]-1,3,5-triazine (**8**) (Continued).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
114.0470	114.0469	3	C_9H_6	
106.5457	213.0902	5	$C_{12}H_{11}N_3O$ (d. i.)	
102.0375	102.0344	2	C_7H_4N	
101.0387	101.0391	13	C_8H_5	
92.0251	92.0262	4	C_6H_4O	
89.0385	89.0391	2	C_7H_5	
77.0381	77.0391	6	C_6H_5	
75.0228	75.0235	9	C_6H_3	
74.0165	74.0156	3	C_6H_2	
64.0620		4		
63.0635		6		
62.0639		2		

7-*p*-Anisyl-2,4-diethylpyrazolo[1,5-*a*]-1,3,5-triazine (**9**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
284.1552	284.1548	2	$C_{14}{}^{13}C_2H_{18}N_4O$	
282.1508	283.1514	21	$C_{15}{}^{13}CH_{18}N_4O$	
282.1489	282.1487	100	$C_{16}H_{18}N_4O$	
281.1382	281.1402	4	$C_{16}H_{17}N_4O$	
229.1151	229.1126	3	$C_{11}{}^{13}C_2H_{13}N_3O$	
228.1107	228.1092	27	$C_{12}{}^{13}CH_{13}N_3O$	
227.1067	227.1059	100	$C_{13}H_{13}N_3O$	M-RCN "A"
226.0965	226.0980	3	$C_{13}H_{12}N_3O$	
212.0782	212.0824	4	$C_{12}H_{10}N_3O$	
173.0687	173.0715	3	$C_{10}H_9N_2O$	
172.0623	172.0637	2	$C_{10}H_8N_2O$	"B"
170.0594	170.0606	12	$C_{11}H_8NO$	"F"
146.0584	146.0592	2	$C_7H_6N_4$	
145.0579	145.0595	4	$C_7{}^{13}CH_6N_3$	
144.0537	144.0575	28	$C_{10}H_8O$	"D"
132.0581	132.0575	2	C_9H_8O	
129.0345	129.0340	5	C_9H_5O	
127.0398	127.0422	3	C_9H_5N	
115.0521	115.0548	10	C_9H_7	
114.0452	114.0469	5	C_9H_6	
113.5544	227.1067	4	$C_{13}H_{13}N_3O$ (d. i.)	
102.0353	102.0344	2	C_7H_4N	
101.0382	101.0391	12	C_8H_5	
92.0262	92.0262	4	C_6H_4O	
89.0390	89.0391	3	C_7H_5	
79.0178	79.0184	2	C_5H_3O	
77.0387	77.0391	5	C_6H_5	Ph

Table I (Continued)

7-*p*-Anisyl-2,4-diethylpyrazolo[1,5-*a*]-1,3,5-triazine (**9**) (Continued).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
75.0226	75.0235	7	C_6H_3	
64.0126		3		
62.9997		5		

2,4-Dimethylpyrazolo[1,5-*a*]-1,3,5-triazine (**10**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
149.0776	149.0782	12	$C_6{}^{13}CH_8N_4$	
148.0739	148.0749	100	$C_7H_8N_4$	$M^{+\cdot}$
124.0738	124.0749	3	$C_5H_8N_4$	
108.0541	108.0517	12	$C_4{}^{13}CH_5N_3$	
107.0491	107.0483	90	$C_5H_5N_3$	M-RCN "A"
106.0415	106.0405	3	$C_5H_4N_3$	
83.0493	83.0483	10	$C_3H_5N_3$	
79.0417	79.0422	10	C_5H_5N	"F"
78.0338	78.0344	6	C_5H_4N	F-1
66.0325	66.0344	10	C_4H_4N	

4-Methyl-2-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**11**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
211.0919	211.0984	17	$C_{11}{}^{13}CH_{10}N_4$	
210.0860	210.0905	100	$C_{12}H_{10}N_4$	$M^{+\cdot}$
170.0677	170.0673	6	$C_9{}^{13}CH_7N_3$	
169.0632	169.0640	35	$C_{10}H_7N_3$	M-RCN "A"
141.0556	141.0578	17	$C_{10}H_7N$	"F"
140.0483	140.0500	14	$C_{10}H_6N$	F-1
114.0483	115.0422	7	C_8H_5N	
108.0543	108.0562	2	$C_5H_6N_3$	
107.0474	107.0483	5	$C_5H_5N_3$	
104.0490	104.0500	3	C_7H_6N	
103.0414	103.0422	7	C_7H_5N	PhCN
89.0388	89.0391	2	C_7H_5	"E"
77.0376	77.0391	19	C_6H_5	Ph
76.0303	76.0313	4	C_6H_4	
70.5291	141.0556	2	$C_{10}H_7N$ (d. i.)	
66.0246	67.0296	3	$C_3H_3N_2$	
63.0288		2		

4-Ethyl-2-methyl-8-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**12**).

Mass Measured	Mass Calcd.	Intensity	Formula	Assignment
239.1252	239.1252	18	$C_{13}{}^{13}CH_{14}N_4$	
238.1207	238.1218	100	$C_{14}H_{14}N_4$	$M^{+\cdot}$
237.1096	237.1140	2	$C_{14}H_{13}N_4$	M-1
224.1060	224.1062	4	$C_{13}H_{12}N_4$	
196.0865	196.0875	3	$C_{12}H_{10}N_3$	
184.0871	184.0875	9	$C_{11}H_{10}N_3$	
183.0792	183.0796	5	$C_{11}H_9N_3$	M-RCN "A"
182.0714	182.0718	2	$C_{11}H_8N_3$	
159.0794	159.0796	2	$C_9H_9N_3$	
155.0637	155.0609	4	$C_{10}H_7N_2$	
154.0636	154.0657	11	$C_{11}H_8N$	
143.0575	143.0564	4	$C_8{}^{13}CH_6N_2$	
142.0522	142.0531	11	$C_9H_6N_2$	"B"
140.0484	140.0500	16	$C_{10}H_6N$	"F"
129.0578	129.0578	2	C_9H_7N	
116.0482	116.0500	3	C_8H_6N	
114.0436	114.0429	21	C_9H_6	"D"
113.0389	113.0391	4	C_9H_5	
89.0377	89.0391	4	C_7H_5	
88.0326	88.0313	7	C_7H_4	"E"
77.0385	77.0391	2	C_6H_5	Ph

Table II

New Pyrazolo[1,5-*a*]-1,3,5-triazines

Compound No.	Solvent of recrystallization	m.p.°	Yield %	Formula	C	H	N	C	H	N
2	Benzene	164.5-165	83	$C_{13}H_{12}N_4$	69.61	5.40	24.99	69.55	5.52	25.19
3	*n*-Heptane	93-95	71	$C_{14}H_{14}N_4$	70.55	5.93	23.51	70.57	6.03	23.59
5	*n*-Hexane	112-113	73	$C_{15}H_{16}N_4$	71.40	6.39	22.21	71.52	6.34	22.31
6	Ethanol	183-185	46	$C_{18}H_{14}N_4$	75.50	4.93	19.57	75.20	4.98	19.78
7	DMF	160-162	53	$C_{18}H_{14}N_4$	75.50	4.93	19.57	75.60	5.01	19.63
8	Petroleum ether (a)	148-150	72	$C_{15}H_{16}N_4O$	67.16	5.97	20.89	67.32	6.02	21.03
9	Petroleum ether (a)	115-116	59	$C_{16}H_{18}N_4O$	68.08	6.38	19.85	68.31	6.50	20.06
11	Ethanol	117-119	25	$C_{12}H_{10}N_4$	68.54	4.80	26.65	68.60	4.75	26.63
12	*n*-Hexane	83-84	64	$C_{14}H_{14}N_4$	70.55	5.93	23.51	70.31	6.08	23.32

(a) B.p. 30-60°.

bitors, which have potential in several areas of pharmacology (10, 11).

EXPERIMENTAL

The electron-impact mass spectra were obtained by using an AEI MS-902 mass spectrometer operated at an effective resolving power of approximately 15,000. The samples were introduced into the ion source by means of a direct-insertion probe while simultaneously bleeding in the reference compound, perfluorotributylamine. Repetitive scans were made at a scan rate of 40 seconds per mass decade while the sample probe was heated from room temperature to about 200°. The signal output from the mass spectrometer was digitized and recorded on magnetic tape for subsequent computer processing. Relative intensities and mass measurements are give in table I.

The MS-902 is equipped with an SRIC CIS-2 ion source which can be operated in either the electron-impact or chemical-ionization mode. The spectra were recorded at 70-eV, and the ion source temperature was maintained at 150°.

The pyrazolo[1,5-*a*]-1,3,5-triazines used in these experiments were analytically pure; compounds **1**, and **2** and **10** have been previously described in references 5 and 8. The other compounds were prepared by the same method used in our previous publication (9); their properties are given in table II.

Micro-analyses were preformed by Heterocyclic Chemical Corporation of Harrisonville, Missouri and by Galbraith Labs., Knoxville, Tennessee.

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