Probable Formation of Cyclobutadiene-Type Cations in the Mass-Spectral Decomposition of Pyridazines and Tetrazines[1,2]

Stephen J. Weininger[3] and Edward R. Thornton

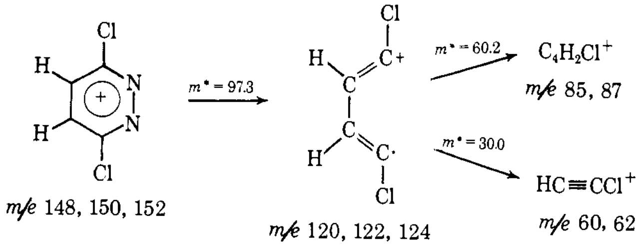
Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, and the Division of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts. *Received December 5, 1966*

Abstract: After their formation by electron impact, most of the molecular ions of 3,6-dichloropyridazine lose nitrogen to form $C_4H_2Cl_2^+$. The dichloroacetylene ion $C_2Cl_2^+$ is observed, in low abundance, even at low ionizing voltages. This raises the possibility that the $C_4H_2Cl_2^+$ ion has the dichlorocyclobutadiene structure. This hypothesis is rendered more plausible by the relatively high ion current due to $C_2H_2^+$; the unusually intense peak due to the doubly charged ion $C_4H_2Cl_2^{2+}$ is readily explained if it has the cyclobutadiene structure. The mass spectra of *s*-tetrazine and 3,6-dimethyl-*s*-tetrazine include low-intensity peaks due to acetylene cation and dimethylacetylene cation, respectively. The bond formation between carbon atoms 3 and 6 is most easily explained if a diazacyclobutadiene cation intervenes. Acetylene ions are virtually absent in the mass spectra of 3,6-dicyano- and 3,6-bis(trifluoromethyl)-*s*-tetrazine. The spectra of all these compounds are discussed in detail. The question of cyclobutadiene formation in the mass spectral decomposition of other aromatic molecules is considered.

The frequently decisive effect of stable *neutral* molecule formation upon mass spectral patterns has been well documented.[4] The present investigation was concerned with the loss of nitrogen from cyclic molecules with consequent disruption of the ring. One of the most interesting questions concerning the fate of the remaining fragment is whether or not it recyclizes. In order to clarify these and other points, the mass spectra of several derivatives of *s*-tetrazine and that of 3,6-dichloropyridazine were obtained and analyzed.

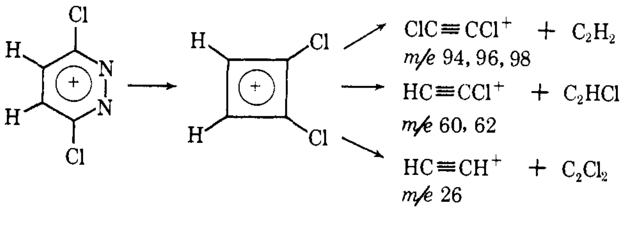
Some time after the completion of our work a paper appeared describing the mass spectra of benzene, pyridine, and the three isomeric diazines, all obtained with a high-resolution instrument.[5] The most abundant fragment ion in the mass spectrum of pyridine is that derived by loss of HCN from the molecular ion; in similar fashion, loss of N_2 is the most important fragmentation process in the case of pyridazine. The alternative losses of C_2H_2 and HCN, respectively, are much less probable; these data reflect the relative thermodynamic stabilities of HCN *vs.* C_2H_2 and N_2 *vs.* HCN. The mass spectra of 2-methylpyrazine and tetramethylpyrazine also accord with the supposition that the thermodynamically most stable neutral fragment will have the greatest probability of being ejected.[6]

The mass spectrum of 3,6-dichloropyridazine (Figure 1) contains many features which one might expect on the basis of the foregoing discussion. The molecular ion peaks are prominent, as are those corresponding to the fragment $C_4H_2Cl_2^+$ formed by loss of N_2 from the molecular ion. At lower mass one encounters peaks at *m/e* 85 and 87 ($C_4H_2Cl^+$; *m/e* 85 is the base peak) and *m/e* 60 (C_2HCl^+). The data would all seem to be compatible with the following simple scheme



All the indicated metastable peaks have been observed,[7] except perhaps that arising from formation of $HC\equiv CCl^+$; the interpretation is somewhat complicated because metastable peaks for the reaction $C_4H_2Cl^+ \rightarrow C_4H_2^+ + Cl\cdot$ would occur theoretically at *m/e* 28.7 and 29.4. In fact, metastables corresponding to both processes seem to be present. The molecular compositions of all fragments noted were confirmed by high-resolution measurements.

There are three peaks at *m/e* 94, 96, and 98, corresponding to $C_2Cl_2^+$ ions of varying isotopic composition. These peaks persist in the spectrum down to fairly low ionizing voltages. If we discount for the moment the possibility of chlorine rearrangement, then the most reasonable explanation for the formation of $C_2Cl_2^+$ involves the assumption that the ion $C_4H_2Cl_2^+$ has the cyclobutadiene structure. The peak at *m/e* 26 has been shown by exact mass measurement to be due almost solely to $C_2H_2^+$ ions. Since most molecular ions lose N_2 initially,[5] the formation of $C_2H_2^+$ in reasonable abund-



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(1) For further details, *cf.* S. J. Weininger, Ph.D. Dissertation, University of Pennsylvania, 1964; available from University Microfilms, Ann Arbor, Mich.; *Dissertation Abstr.*, 25, 6976 (1965).

(2) Supported in part by Public Health Service Grant 10693 from the National Institute of General Medical Sciences, to the University of Pennsylvania.

(3) Socony-Mobil Fellow, 1962–1964, University of Pennsylvania.

(4) F. W. McLafferty in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 326.

(5) J. Momigny, J. Urbain, and H. Wankenne, *Bull Soc. Roy. Sci. Liege*, 34, 337 (1965).

(6) American Petroleum Institute, Research Project 44, Catalog of Mass Spectral Data, No. 1417 and 1350.

(7) Only those metastable ions corresponding to transitions between the isotopically most abundant species have been shown for the sake of clarity. In general, several metastable peaks were observed for each process.

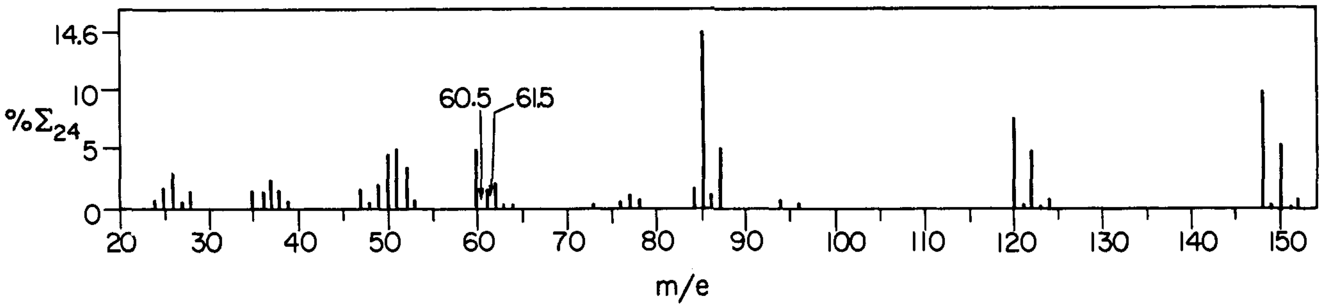
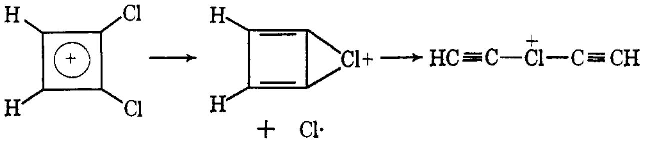


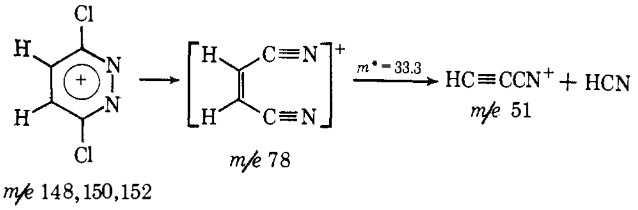
Figure 1. Mass spectrum of 3,6-dichloropyridazine.

ance would seem to require that the remaining carbon atoms become bonded to one another, as provided for by the cyclobutadiene cation. Corroborative evidence for the proposed structure of this ion is provided by the intensity of the peaks at *m/e* 60.5, 61.5, and 62.5, which correspond to ions having the formula $^{12}C_3{}^{13}CH_2Cl_2{}^{2+}$ and varying in chlorine isotope composition. These doubly charged ions are 20–30% as intense as the singly charged ones of identical composition. In general, doubly charged ions are usually no more than 1% as intense as their singly charged counterparts; this is indeed the case with 3,6-dichloropyridazine molecular ion. According to very simple molecular orbital theory, in the ground state of cyclobutadiene two electrons are in nonbonding orbitals.[8] Thus, the second ionization potential, as well as the first, should be unusually low for cyclobutadiene; if our theory is correct, the comparatively high abundance of $C_4H_2Cl_2{}^{2+}$ ions would be readily comprehensible.

The ion $C_4H_2Cl^+$ is the most abundant one in the spectrum, and one would like to know what structural features make this ion particularly stable, other than the fact that it is an even-electron ion.[9] The ion might well be acyclic, the loss of Cl providing an opportunity to open the ring, with consequent strain relief. It is noteworthy that the peaks at *m/e* 42.5 and 43.5 ($C_4H_2Cl^{2+}$) are only 1% as intense as those at *m/e* 85 and 87. It is intriguing (though highly speculative) to suggest that $C_4H_2Cl^+$ is a chloronium ion, with two acetylenyl groups bonded to chlorine. This arrangement has the merits of maximum covalency for all the atoms, as well as permitting charge dispersal through overlap of the acetylenic π orbitals with the d orbitals of the chlorine atom. Its formation from dichlorocyclobutadiene cation is readily envisaged as



Some 3,6-dichloropyridazine molecular ions seem to lose both chlorine atoms to form $C_4H_2N_2{}^+$, the latter then decomposing further to C_3NH^+. The occurrence of the second process is indicated by a metastable peak at *m/e* 33.3; the composition of the ions has been established by exact mass measurements. A probable scheme is depicted as



Because of the possibility of hydrogen and chlorine rearrangement, the intermediacy of a cyclobutadiene cation in the mass spectral decomposition of 3,6-dichloropyridazine has not been unequivocally established. (The spectra of pyridazine, pyrimidine, and pyrazine are each distinctive and different,[5] which would seem to rule out extensive scrambling of the *skeletal* atoms.) We therefore sought a six-membered ring system such that substituents in the 1 and 4 positions could not become part of the same acetylenic ion unless the ring atoms 1 and 4 became bonded. The *s*-tetrazines (I) seemed ideal for fulfilling this criterion. The

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mass spectrum of *s*-tetrazine (I, X = H) itself is relatively simple (Table I): an intense molecular ion peak followed by peaks corresponding to M − 28 and M − 29. The latter is larger than the former, a situation also found in the mass spectrum of pyridazine. By analogy, these peaks must arise from loss of N_2, and N_2 plus H, respectively. Loss of HCN from the molecular ion is less than one-tenth as favorable as loss of N_2. The largest peaks occur at *m/e* 27 (HCN^+) and *m/e* 28 (HCN^+H

Table I. Mass Spectrum of *s*-Tetrazine[a,b]

m/e	%Σ_{24}	*m/e*	%Σ_{24}
24	0.21	42	0.17
25	0.37	43	0.10
26	3.99	52	0.11
27	31.25	53	2.13
28	41.10	54	1.30
29	1.06	55	0.12
40	0.41	82	15.44
41	0.93	83	0.58

[a] Intensities in this and subsequent tables are uncorrected. [b] Only those ions that have a %Σ_{24} value greater than 0.10 are included, unless the ion is of particular significance.

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(8) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin Inc., New York, N. Y., 1961, p 73.

(9) Reference 4, p 318.

and N_2^+); there is also a less prominent peak at *m/e* 29 (N_2^+H). The intermediacy of a four-membered cyclic ion is indicated by peaks at *m/e* 24 (C_2^+) and *m/e* 25 (C_2H^+). There is a considerable ion current at *m/e* 26, but in the absence of high-resolution measurements it is not possible to say what percentage is due to $C_2H_2^+$ ions and what percentage to CN^+.

The spectra of three additional tetrazines (Tables II–IV) were examined in a search for additional evidence of a cyclic intermediate. The initial mode of fragmentation of 3,6-dimethyl-*s*-tetrazine (I, X = CH_3) involves the loss of N_2, as might be expected. The fragment ion, $C_4H_6N_2^+$ (*m/e* 82), follows a minor decomposition path involving loss of CH_3. Its major fragmentation mode leads principally to $C_2H_4N^+$, as well as $C_2H_3N^+$ and $C_2H_2N^+$ in somewhat lesser abundance. The $C_2H_4N^+$ ion very likely has the structure $CH_3C{\equiv}N^+H$, since this is an even-electron ion having maximum covalency for all the elements. There is a sizable metastable peak in the region of *m/e* 5.5 (it is difficult to establish the exact mass number in this part of the spectrum[10]), which would seem to indicate that the $CH_3C{\equiv}N^+H$ and CH_3CN^+ ions decompose further, forming CH_3^+.

Table II. Mass Spectrum of 3,6-Dimethyl-*s*-tetrazine

m/e	$\%\Sigma_{24}$	*m/e*	$\%\Sigma_{24}$
24	0.38	42	42.25
25	1.59	43	1.09
26	4.47	51	0.12
27	3.24	52	0.22
28	3.96	53	0.26
29	0.36	54	0.35
38	2.13	67	0.50
39	3.54	82	0.48
40	12.14	110	4.91
41	17.34	111	0.29

Table III. Mass Spectrum 3,6-Dicyano-*s*-tetrazine[a]

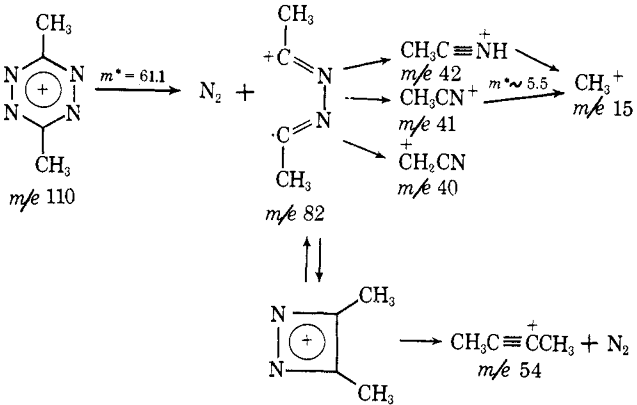
m/e	$\%\Sigma_{24}$	*m/e*	$\%\Sigma_{24}$
24	7.09	52	52.66
25	0.16	76	0.08
26	10.41	78	0.10
28	23.04	104	0.33
38	4.48	132	1.04

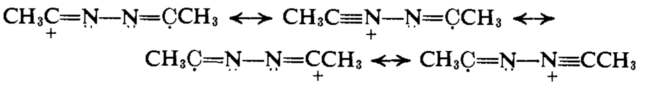
[a] Approximate spectrum; see Experimental Section.

Table IV. Mass Spectrum of 3,6-Bis(trifluoromethyl)-*s*-tetrazine

m/e	$\%\Sigma_{24}$	*m/e*	$\%\Sigma_{24}$
24	0.74	61	0.11
26	1.26	62	0.27
29	0.73	69	55.34
31	9.16	70	1.04
36	0.10	76	7.77
38	0.37	77	0.25
40	0.22	95	0.12
43	0.53	102	0.36
44	0.74	121	5.12
45	0.12	122	0.18
50	8.16	130	0.12
51	0.39	141	0.16
52	0.18	190	0.05
54	0.23	192	0.03
57	0.28	218	2.42

Exact mass measurements have established the composition of the ion giving the *m/e* 54 peak as $C_4H_6^+$. It seems very plausible that this is a dimethylacetylene ion arising from decomposition of dimethyldiazacyclobutadiene cation.[11] The low ion current at *m/e* 54 may indicate that relatively few molecules decompose *via* the cyclic intermediate, which fact may be ascribed to resonance stabilization of the open-chain form. Such stabilization is not possible in an all-carbon chain.





$$CH_3\underset{+}{C}{=}\underset{\cdot\cdot}{N}{-}\underset{\cdot\cdot}{N}{=}\underset{\cdot}{C}CH_3 \longleftrightarrow CH_3C{\equiv}\underset{+}{N}{-}\underset{\cdot\cdot}{N}{=}\underset{\cdot}{C}CH_3 \longleftrightarrow$$

$$CH_3\underset{\cdot}{C}{=}\underset{\cdot\cdot}{N}{-}\underset{\cdot\cdot}{N}{=}\underset{+}{C}CH_3 \longleftrightarrow CH_3\underset{\cdot}{C}{=}\underset{\cdot\cdot}{N}{-}\underset{+}{N}{\equiv}CCH_3$$

It was not possible to obtain a spectrum of pure 3,6-dicyano-*s*-tetrazine (I, X = CN), since this material was too involatile to be purified by the usual vacuum-line techniques. As the tetrazine has a molecular formula C_4N_6, it is quite easy to identify peaks due to impurities. By obtaining spectra under a variety of conditions and comparing them, it was possible to compile a set of data which gives a good qualitative idea of the decomposition pattern of dicyanotetrazine. A relatively weak M − N_2 peak is observed, together with a small peak corresponding to $(NC{-}C{\equiv}C{-}CN)^+$. The most intense peak is that corresponding to the cyanogen cation, $(CN)_2^+$; the N_2^+ peak is also quite intense. The decomposition of 3,6-bis(trifluoromethyl)-*s*-tetrazine (I, X = CF_3) is influenced most strongly by the CF_3 groups—the most intense peaks are those corresponding to CF_3^+, CF_2^+, and CF^+. There is no observable peak arising from the $(CF_3C{\equiv}CCF_3)^+$ ion, and that due to the M − N_2 ion is just detectable. There are sizable peaks from the CF_2CN^+ and $C_3F_3N_2^+$ ions. The latter seems analogous to the $C_3H_3N_2^+$ and $C_3N_3^+$ ions in the mass spectra of dimethyl- and dicyanotetrazine; they probably all have the structure $Y{\equiv}CC{\equiv}N^+N{=}C$ (Y = H_3, F_3, N). There seems to be little or no tendency for the M − N_2 intermediate from dicyano- and bis(trifluoromethyl)tetrazine to cyclize; whether this fact can be ascribed to the electron-withdrawing tendencies of the CF_3 and CN substituents is a moot point.

Evidence relating to the occurrence of four-membered cyclic intermediates in the mass-spectral decomposition

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(10) The *m/e* value was arrived at (1) by interpolation from the start of the scan, and (2) by calculating the distance covered by a decade and then computing the position of *m/e* 6 from that of *m/e* 12. Both methods gave the same results.

(11) The mass spectra of the azines of benzaldehyde, cyclopropylcarboxaldehyde, and several others exhibit peaks due to M − N_2 ions. These would seem to argue for the intermediacy of diazacyclobutene cations: E. P. Smith, unpublished observations, University of Pennsylvania.

of six-membered rings is scarce. Momigny and Wirtz-Cordier,[12] in their study of the isomeric difluorobenzenes, noted that the $C_2F_2^+$ ion was most abundant in the spectrum of the *ortho* isomer, and that its abundance in the spectra of the *meta* and *para* isomers was identical. This evidence militates against the difluorocyclobutadiene cation as a fragmentation product in the mass spectra of these compounds. The relative abundance of the ions C_2HF^+ in the three spectra is also consistent with this view. A study of $C_4H_4^+$ ions produced from various sources[13] has shown that these ions may be divided into three classes, depending on their ΔE_f (the energy of formation in the gas phase from the elements). The ions from benzene, hexa-3,5-dienyne, and butadiene have the highest ΔE_f, about 14.14 ev. The $C_4H_4^+$ ion from pyridazine falls into the same category, since its ΔE_f is 14.52 ev; the ion of identical composition from pyridine has a considerably lower value (13.70 ev).[5] If some decompositions proceed by way of cyclic $C_4H_4^+$ ions and some by way of acyclic species, then such a variation in ΔF_f is readily understandable; at the moment, however, there is no way of correlating structure and ΔF_f. Momigny, Brakier, and D'Or[13] assume that the ions having a $\Delta E_f \geq 14.15$ ev have the structure $\underset{\cdot}{C}H{=}CHCH{=}\overset{+}{C}H$, on the basis of the structures of the neutral molecules which give rise to them. This conclusion is by no means necessary, however.

Beynon and Williams, in their well-known study of the mass spectra of quinones,[14] showed that anthraquinone loses two molecules of carbon monoxide successively upon electron impact to yield, presumably, the biphenylene cation. They also report, without comment, the mass spectrum of *p*-benzoquinone, in which an ion at *m/e* 52 is prominent.

The composition of that ion has recently been shown to be $C_4H_4^+$ by exact mass measurement.[15] Many naphthoquinones lose two molecules of carbon monoxide to form cations whose molecular formulas correspond to those of benzcyclobutadiene cations.[16] Similarly, $C_4F_4^+$ has been established as a prominent ion in the mass spectrum of tetrafluorobenzoquinone.[17] While carbon monoxide seems to be a good "leaving group" in these processes (it is readily lost from tetracyclone upon electron impact[18]), carbon dioxide seems not to be favored, as indicated by the lack of importance of M − 44 compared with the M − 28 ion in the mass spectrum of 2-pyrone.[19]

Experimental Section

The recorded mass spectra were obtained with a CEC Model 21-130 mass spectrometer at a nominal ionizing voltage of 76 v. Exact mass measurements were performed with a CEC Model 21-110, and the metastable peaks were recorded on a Hitachi Model RMU-6.[20] Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer.

3,6-Dichloropyridazine (Aldrich) was recrystallized from hexane, mp 69–70°, lit.[21] 69–70°. Its mass spectrum was completely consistent with its structure.

***s*-Tetrazine** was prepared according to the prescription of Spencer, Cross, and Wiberg.[22] Ethyl diazoacetate (60 g, 0.53 mole) was dimerized and saponified in hot concentrated sodium hydroxide solution. The product, containing sodium dihydro-*s*-tetrazine-3,6-dicarboxylate, was acidified; the bright yellow dihydro-*s*-tetrazine-3,6-dicarboxylic acid was then oxidized with sodium nitrite and sodium acetate and then reacidified, giving *s*-tetrazine-3,6-dicarboxylic acid as a red powder, yield 1.5 g (3%). It decomposed to a black tar at 155–160°, depositing small ruby-red crystals in the cool portion of the capillary, lit.[23] mp 148° dec.

The diacid was ground with five times its weight of sand and decarboxylated in a vacuum sublimator at 160° and 0.01–0.1 mm. The crystalline sublimate was transferred at −196° to a tube having a stopcock and a joint which fitted the inlet system of the mass spectrometer. The tube was warmed to 0° and evacuated for several minutes to remove volatile impurities. It was stored under vacuum in the refrigerator in the absence of light. Its mass spectrum remained essentially unchanged after 3 months except for the appearance of a small peak at *m/e* 45 (possibly formamide).

3,6-Dimethyl-*s*-tetrazine. Ethyl iminoacetate hydrochloride[24] (90 g, 0.73 mole) was condensed with anhydrous hydrazine (25 g, 0.78 mole) in absolute ethanol at −50°.[25] The product, 3,6-dimethyl-1,2-dihydro-*s*-tetrazine, was oxidized with sodium nitrite and aqueous acetic acid, and the red-violet 3,6-dimethyl-*s*-tetrazine was extracted with 600 ml of methylene chloride. Most of the solvent was removed by distillation until the extract was 15 ml in volume.

The compound could not be satisfactorily purified by either column chromatography or gas–liquid chromatography. The most satisfactory method was bulb-to-bulb distillation under high vacuum. A few milliliters of the methylene chloride solution was distilled into a trap held at −46°, which allowed the solvent to pass through. An oily involatile residue remained behind. Several repetitions of this procedure freed the compound of methylene chloride. The colored material was next sublimed into a trap held at −23°, which held the tetrazine but allowed a colorless impurity to pass through. After several purifications at this temperature, the tetrazine exhibited in its mass spectrum no peaks inconsistent with its molecular formula.

3,6-Dicyano-*s*-tetrazine. Ethyl diazoacetate (30 g, 0.26 mole) was dimerized in liquid ammonia (60 ml) in a sealed Carius tube for 4 days at room temperature,[26] yielding the ammonia complex of 1,2-dihydro-*s*-tetrazine-3,6-dicarboxamide, 20 g, 42%. Oxidation with sodium nitrite and acetic acid gave *s*-tetrazine-3,6-dicarboxamide, which charred but did not melt up to 280°.

Several hundred milligrams of the dicarboxamide was mixed with five times its weight of phosphorus pentoxide and dehydrated at 150–160° and 0.01–0.05 mm in a vacuum sublimator.[27] The orange solid which collected on the cold finger was involatile and could only be sublimed with the aid of a hot air gun even at 10^{-4}–10^{-5} mm. Its mass spectrum was replete with peaks arising from impurities which were easily recognized as such because of the simple molecular formula of the desired material, C_4N_6. Generation of the dicyanotetrazine in an evacuated apparatus separated from the mass spectrometer by only a break-seal still resulted in a spectrum containing many impurity peaks. Several such spectra were recorded and from them, by taking account of variations of related peaks from one spectrum to the next, it was possible to construct an approximate mass spectrum of dicyanotetrazine.

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(20) The exact mass and metastable ion measurements were kindly made by Dr. T. Shannon, through the courtesy of Professor F. W. McLafferty, Purdue University.

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3,6-Bis(trifluoromethyl)-*s*-tetrazine.[28] *s*-Tetrazine-3,6-dicarboxylic acid (1.8 g, 0.01 mole) was loaded into a section of stainless-steel tubing closed at one end with a cap containing a Teflon ring and connected to a high-pressure valve which carried a metal ball joint. The bomb, of 15–20 ml capacity, was evacuated and sulfur tetrafluoride[29] (6.5 g, 0.06 mole, an excess) was condensed into it at −196°. The bomb was heated at 75° for 10 hr.

After cooling to room temperature the bomb was attached to a vacuum manifold and its contents pumped through three traps in series, the first two at −78° and the last at −196°. The contents of the last trap, which was a mixture of sulfur tetrafluoride, thionyl fluoride, and silicon tetrafluoride, was returned to the bomb, which still contained nonvolatile material. It was further heated at 100° for 8 hr. The contents was fractionated as before and all the material condensed at −78° combined. This mixture was orange in color and obviously contained hydrogen fluoride, as it etched the glass trap upon warming. The mixture was allowed to sublime four times under vacuum through a glass tube packed with sodium fluoride and silica gel. Some material remained adsorbed on the silica gel. The volatile fraction was free of hydrogen fluoride and water as evidenced by its infrared spectrum. The highest peak in its mass spectrum was at *m/e* 218, and the spectrum was completely consistent with that expected for bis(trifluoromethyl)-*s*-tetrazine.

An additional quantity of the tetrazine could be obtained by extraction of the sodium fluoride–silica gel with methylene chloride, concentration of the extract by fractionation of the solvent through a spinning-band column, and subsequent purification by bulb-to-bulb distillation at −30°. The orange, thermochromic compound had prominent infrared absorptions (gas phase) at 1428, 1323, 1207, 1190, 1165, 1148, 1067, 769, and 764 cm^{-1}.

Anal. Calcd for $C_4F_6N_4$: C, 22.02; F, 52.29; N, 25.69. Found: C, 22.35; F, 52.43; N, 24.44.

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[28] This synthesis was carried out as a joint project with Mr. Ronald Kent, University of Pennsylvania.

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Triarylmethyl Radicals. Synthesis and Electron Spin Resonance Studies of Sesquixanthydryl Dimer and Related Compounds[1]

M. J. Sabacky, C. S. Johnson, Jr., R. G. Smith,
H. S. Gutowsky, and J. C. Martin

Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61803. Received July 29, 1966

Abstract: Factors influencing the dissociation of hexaarylethane into triarylmethyl radicals have been illustrated through synthesis and electron spin resonance (esr) studies of two novel triarylmethyl derivatives. Radical II, 2,6,2′,6′,2′′,6′′-hexamethoxytriphenylmethyl, is extremely hindered toward attack at the central carbon atom, reacting only slowly with oxygen. There is no evidence of dimerization, even in the solid state. Evidence for a pronounced angle (~50°) of twisting of the aryl rings from the plane defined by the central carbon and the three carbons bonded to it is seen in the esr hyperfine interaction with the *para* protons ($a_{para} = 2.26 \pm 0.02$ gauss, compared with 2.77 gauss for the unsubstituted triphenylmethyl). Additional evidence for the larger angle of twist is supplied by the large ^{13}C hfs constant (26 gauss) found in radical II enriched with ^{13}C at the central carbon. The importance of steric interactions in promoting dissociation of hexaarylethanes is reflected in the stability of sesquixanthydryl dimer (III) which is undissociated in the solid and essentially undissociated in solution. Only very weak esr signals could be obtained from solutions of III.

Two principal factors have been postulated to provide the primary driving force for the dissociation of hexaarylethanes to yield free radicals: (a) the resonance stabilization of the radical, and (b) the relief upon dissociation of steric interactions between aryl groups either on the same carbon or on adjacent carbons in the ethane. Estimates[2] of the relative importance of these two factors, based on thermochemical data for the unsubstituted hexaphenylethane, suggest that the resonance effect (50–55 kcal/mole) is about twice as important as the steric effect (17–22 kcal/mole) in promoting the dissociation of this ethane, relative to the dissociation of ethane itself to give two methyl radicals. Many existing data[3] provide qualitative support for the suggested important contributions from each of these effects. The novel free radicals I and II, accessible by reduction of the corresponding carbonium ions,[4] provide extreme cases for the further elucidation of the factors governing the dissociation.

The sesquixanthydryl radical (I) provides a minimum of steric hindrance to dimerization, and the postulated coplanar structure of the radical provides the optimum geometry for delocalization of the odd electron. Radical II, bearing six *o*-methoxy substituents, is expected to have a relatively large angle of twist of the phenyl groups (pitch of the propeller) in its most stable con-

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[1] Taken in part from the Ph.D. Theses of M. J. S. and R. G. S., University of Illinois.

[2] H. E. Bent and F. R. Cuthbertson, *J. Am. Chem. Soc.*, **58**, 170 (1936); J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, Chapter I; J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 18.

[3] G. Wheland, "Advanced Organic Chemistry," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1960: (a) pp 763 ff; (b) p 784; (c) p 779.

[4] J. C. Martin and R. G. Smith, *J. Am. Chem. Soc.*, **86**, 2252 (1964).