H, 6.65; O, 22.87; N, 6.16; S, 3.52. Found: C, 60.90, 61.23; H, 6.52, 6.52; O, 22.86; N, 6.07, 6.15; S, 3.43. Analytical data for leurosine and vincaleukoblastine are in agreement with a tentative formulation as isomeric $C_{46}H_{58}O_9N_4$ compounds.[6] Their ultraviolet spectra are superimposable: λ_{max}^{EtOH} 214 mμ (log a_M 4.74), 259 mμ (log a_M 4.22), and λ_{min}^{EtOH} 246 mμ (log a_M 4.14); shoulders at 288 mμ (log a_M 4.15) and 296 mμ (log a_M 4.12).

The close structural relationship of these two alkaloids is demonstrated further by their essentially identical infrared spectra. The major differences occur in the hydroxyl region of vincaleukoblastine with additional bands at 2.80 and 9.91 μ.[7]

[6] An alternate C_{23} formulation was discarded on the basis of electrometric titrations, carbon-oxygen ratios and functional group analyses as presented in the following communication.

[7] For these spectra, see communication IV, p. 4745.

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RECEIVED JULY 6, 1959

THE DIRECT FLUORINATION OF UREA: THE SYNTHESIS AND PROPERTIES OF DIFLUORAMINE

Sir:

The direct fluorination of urea at 0° yields a complex yellow, corrosive liquid which contains up to 16% active fluorine (to HI) and about 45–55% total fluorine. On solution in water, ammonium fluoride, biurea and unidentified refractory solids are obtained.[1] Distillation of the liquid from Kel-F or polyethylene into glass yields, in the more volatile fraction, CO_2, SiF_4, HNCO, COF_2 and difluoramine, HNF_2.[2] As high as 15% of the original fluorine has been recovered as difluoramine.

Ruff and Staub[3] first reported the preparation of difluoramine but gave no analysis and erroneous physical properties. They also reported that it did not react with aqueous hydriodic acid, which we observed. Therefore, we agree with Kennedy and Colburn[2] that the material described by Ruff and Staub was not difluoramine. Our vapor pressure data agree with Kennedy and Colburn's within experimental error and the infrared spectra are identical. However, our mass spectrum and melting point do differ.

We found that gaseous difluoramine loses hydrogen on contact with various solids to form the recently reported tetrafluorohydrazine.[4] With lithium hydride as a catalyst, yields of 70% are obtained easily. When chilled to −196°, solid difluoramine tends to detonate spontaneously. Chilling only to −142° and working with small samples, minimizes this tendency, but the violence of the reaction requires adequate precautions be taken. Physical properties we determined are listed in Table I.

TABLE I

THE PHYSICAL PROPERTIES OF DIFLUORAMINE

Melting point, °C.	−116 ± 3°
Boiling point, °C.	−23.6°
Density	$d = 1.424 - 0.00202t$
Trouton constant	23.7

Difluoramine was identified by its molecular weight (calculated for HNF_2, 53.02; observed, 54) and its almost instantaneous and quantitative reaction with 0.75 *N* HI according to the equation

$$HNF_2 + 4HI \longrightarrow 2I_2 + NH_4F + HF$$

The mass spectrum taken with a CEC Model 103C mass spectrometer (Table II) is consistent with the above formulation. All of these peaks are reproducible on different samples.

TABLE II

MASS SPECTRUM OF DIFLUORAMINE

m/e	Pattern coef.	+ Ion
14	19.37	N
15	10.50	HN
19	6.89	F
20	1.95	HF
28	1.61	N_2
33	34.35	NF
34	100.00	HNF
52	1.5	NF_2
53	66.97	HNF_2

Sensitivity *n*-butane *m/e* 43 = 69.89 div./μ.
Sensitivity HNF_2 *m/e* 34 = 23.12 div./μ.
Ionizing voltage 70 v.
Ionizing current 10 μa.

The authors are indebted to the Office of Naval Research for support of this work. The mass spectral determination was performed by Mr. Mario Stevens of this laboratory. Mr. Martin Epstein participated in the initial work.

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RECEIVED MAY 11, 1959

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[1] O. Glemser and H. Ludemann, *Z. anorg. allgem. Chem.*, **286**, 168 (1956).

[2] A. Kennedy and C. Colburn, THIS JOURNAL, **81**, 2906 (1959).

[3] O. Ruff and L. Staub, *Z. anorg. allgem. Chem.*, **198**, 32 (1931).

[4] C. B. Colburn and A. Kennedy, THIS JOURNAL, **80**, 5004 (1958).

UNSATURATED MACROCYCLIC COMPOUNDS. XI.[1] CYCLOTETRACOSA-1,3,7,9,13,15,19,21-OCTAENE-5,11,17,23-TETRAYNE AND CYCLOTETRACOSA-1,3,5,7,9,11,13,15,17,19,21,23-DODECAENE

Sir:

We wish to report the synthesis of the completely conjugated 24-membered ring cyclic systems named in the title.

Cyclotetracosa-1,3,7,9,13,15,19,21-octayne (I) (the cyclic "tetramer" of 1,5-hexadiyne)[2] on treatment with potassium *t*-butoxide in *t*-butanol–benzene at 90° for 30 minutes underwent a similar rearrangement to that of the corresponding "trimer."[3] The product, formed in *ca.* 40% yield, was obtained as dark purple prisms from ether (red in solution), which decomposed when heated.

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