added and the ether layer was separated, dried ($MgSO_4$), and filtered. The filtrate was allowed to evaporate to give 3.63 g (90%) of white crystals, mp 100–101 °C (decomp). An analytical sample from CH_2Cl_2 had mp 102–104 °C (decomp).

***1,2-Bis[N,N-bis(2-fluoro-2,2-dinitroethyl)carbamyl]hydrazide* (10).** A solution of 8.0 g (22.8 mmol) of **4** in 40 mL of ether was rapidly stirred in a water bath at 25 °C while 2.7 g of hydrazine hydrate (85% solution) was added dropwise over a 35-min period. After an additional 10 min cold water (50 mL) was added and the ether layer was separated, dried ($MgSO_4$), and filtered. The filtrate was concentrated to 25 mL by distillation, and then $CHCl_3$ was slowly added until the distillate temperature reached 60 °C. After cooling, the crystals were filtered off and then digested with hot CH_2Cl_2 to give 4.23 g (56%) of colorless crystals, mp 195–197 °C (decomp). An analytical sample from ether/$CHCl_3$ melted at 200–201 °C (decomp). The hydrazide **10** was also prepared in 83% yield by treating **9** and **4** in ether solution with pyridine.

***2-[N,N-Bis(2-fluoro-2,2-dinitroethyl)amino]-5,5-dimethyl-1,3,4-Δ^2-oxadiazoline* (11).** Acetone (0.5 mL) was added to a solution of 0.34 g of **9** in 5 mL of ether. Within 5 min, crystals began to precipitate, and after standing overnight the yellow crystals were filtered to give 0.35 g (90%), mp 148–150 °C (decomp). Recrystallization from 1,2-dichloroethane raised the melting point to 151–152 °C (decomp).

***1-[N,N-Bis(2-fluoro-2,2-dinitroethyl)carbamyl]-2-(2-fluoro-2,2-dinitroethanimidoyl)hydrazide* (12).** The hydrazide **9** (1.0 g) was added in 10 portions to a stirred solution of 3.0 g of fluorodinitroacetonitrile[4] in 5 mL of CH_2Cl_2. Crystals began to precipitate within 15 min, and after standing overnight the crystals were removed by filtration and washed with cold CH_2Cl_2. The cream-colored crystals (1.23 g, 86%) melted at 109–110 °C (decomp). Recrystallization did not raise the melting point.

***1-[N,N-Bis(2-fluoro-2,2-dinitroethyl)carbamyl]-2-(2-fluoro-2,2-dinitroacetyl)hydrazide* (13).** The hdyrazide **12** (0.79 g) was stirred with 10 mL of concentrated HCl until dissolved (10 min) after which the solution was allowed to stand overnight. The solution was then diluted with 30 mL of water and extracted with ether. Evaporation of the ether gave 0.68 g of an oily residue which was crystallized from CH_2Cl_2/$CHCl_3$ to give 0.37 g of **13**. Recrystallization from CH_2Cl_2 gave mp 140–141 °C.

***3-[Bis(2-fluoro-2,2-dinitroethyl)amino]-5-(fluorodinitromethyl)-trifluoroacetyl-1,2,4-triazole* (14).** A mixture of 1.12 g of **12** and 10 mL of trifluoroacetic anhydride was stirred at ambient temperature for 48 h. The volatiles were removed with a stream of N_2 and gentle heating (30–35 °C) to give an oil which was dried in a vacuum desiccator over KOH to a constant weight (1.31 g, 100%). The ^1H NMR spectrum ($CDCl_3$) showed a large doublet at 5.16 ppm and much smaller doublets at 4.80 and 4.08 indicating a mixture of isomers differing in the position of the trifluoroacetyl group.

***2,5-Dichloro-1,1,6,6-tetrakis(2-fluoro-2,2-dinitroethyl)-1,3,4,6-tetraazahexa-2,4-diene* (15).** A mixture of 2.66 g of **10**, 2.7 g of PCl_5, and 15 mL of $POCl_3$ was refluxed for 6.5 h. After cooling the mixture was poured into ice water with stirring. When the insoluble material solidified, it was removed by filtration and washed with cold water to give 2.69 g (96%) of a yellow solid, mp 138–142 °C. Recrystallization raised the melting point to 143–145 °C.

***1,2′-Azobis[N,N-bis(2-fluoro-2,2-dinitroethyl)carbamyl]* (16).** A mixture of 4.66 g of **10** and 60 mL of 70% nitric acid was stirred for 5 h at ambient temperature, at which time 80 mL of cold water was added. The product was removed by filtration, washed with water, and dried to yield 4.46 g (96%) of light-orange crystals, mp 158–160 °C (decomp). Recrystallization did not raise the melting point.

***N,N,N′,N′-Tetrakis(2-fluoro-2,2-dinitroethyl)oxamide* (17). Caution!** This experiment should only be done on a small scale since it involves heating a neat explosive to a high temperature. Five samples (0.3 g each) of the azo compound **16** were heated *separately* in an oil bath at 150–160 °C until the color of the melts changed from red to light orange (ca. 20 min). The melts were cooled and were dissolved in ethyl ether. Some unreacted azo compound **16** was removed by filtration, and the filtrate was chromatographed on silica gel. The column was eluted first with benzene and then with 50% CH_2Cl_2/hexane with a gradual increase to 100% CH_2Cl_2. A total of 0.51 g (36%) of white crystals was obtained, mp 90–93 °C. Recrystallization from $CHCl_3$ raised the melting point to 92–94 °C.

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Carbon-13 Nuclear Magnetic Resonance Spectra of 2*H*-Cyclopenta[*d*]pyridazines and Cyclopenta[*c*]thiapyran

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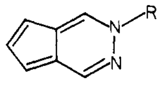
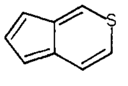
The proton-decoupled ^{13}C NMR spectra of cyclopenta[*d*]pyridazine, its 2-methyl and 2-phenyl derivatives, and cyclopenta[*c*]thiapyran are reported.

Studies on ^{13}C NMR spectra of heterocyclic aromatic compounds (*1–4*) do not seem to have included heteroanalogues of nonbenzenoid hydrocarbons. Compounds I–IV were selected as examples of the latter and their proton-decoupled spectra recorded.



I, R = H
II, R = CH_3
III, R = C_6H_5



IV

The spectrum of I was quite simple. The assignments are given in Table I. The finding of single peaks for the 1 and 4, 5 and 7, and 8 and 9 pairs of carbons had been anticipated

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Table I. ^{13}C NMR Shifts for Azulene and Heteroanalogues[a]

carbon position[b]	azulene[c]	I[d]	II[e]	III[e]	IV[f]
5 (1, 3)	119.2	105.7	106.8	109.2	115.3
7 (1, 3)	119.2	105.7	106.2	107.2	114.2
6 (2)	137.9	130.4	131.0	132.1	117.4
1 (4, 8)	136.9	137.1	134.1	133.4	127.5
4 (4, 8)	136.9	137.1	141.0	141.4	136.1
3					134.4
8 (9, 10)	140.8	121.0	120.4	120.5	139.9
9 (9, 10)	140.8	121.0	121.1	123.2	130.7
10			47.3	145.0	
11, 15				122.8	
12, 14				127.8	
13				129.6	

[a] Relative to Me_4Si (internal reference). [b] Parenthetical numbers are corresponding positions in azulene. [c] Data from ref *14*. [d] Me_2SO-d_6 solvent. [e] $CDCl_3$ solvent. [f] Acetone-d_6 solvent.

since the ^1H NMR spectrum had shown the equivalence of the protons at the 1 and 4 positions and indicated rapid isomerization between the identical tautomers (*5*). The assignment for C-1 and C-4 was based on broadening of the signal by the quadrupoles of the adjacent nitrogens and relative deshielding of carbon directly bonded to nitrogen bearing a partial positive charge. Consideration of the resonance structures of I and qualitative comparisons of the relative intensities and chemical shifts of the 5-, 7-, and 6-carbon absorptions with those of the corresponding positions in azulene were used for the C-5, C-6, and C-7 assignments. The signal for C-8 and C-9 had the lowest intensity.

In the spectrum of II the methyl carbon (C-10) peak was in the region reported for the methyl bonded to a π-excessive aromatic nitrogen (*2*, *6*). The peaks for C-1 and C-4 were selected on the basis of data for the analogous carbons in 1*H*- and 1-methylpyrazoles (*7*) and in 1-methylimidazole (*8*), and because the π-equivalent N-3 was more electron attracting than the π-excessive N-2 (*9*). Support for the latter assertion has been provided by the chemical shifts for H-1 and H-4 as determined by spin-lattice relaxation meaurements (*10*). Spectral comparison with I was used for the C-5, C-6, and C-7 assignments. In the absence of a suitable model, tentative assignments for the quaternary carbons (C-8 and C-9) were made on the basis of the extension of the nitrogen inductive effects. Comparison with the spectra of II, aniline (*11*), and azobenzene (*3*) led to the assignments for III.

Compound IV was unstable in chloroform so the spectrum was taken in hexadeuterioacetone. Support for the initial assignments, especially for C-1 vs. C-3 and C-4, was provided by the multiplicities in the ^1H-^{13}C coupled spectrum. The chemical shift for C-1 corresponded to that reported for C-2 in thiophene (*12*), but both the ^1H and ^{13}C spectra showed the 3 and 4 positions to be relatively less shielded than the corresponding thiophene positions. The C-H coupling constants ranged from 162 to 182 Hz for 1-bond coupling and from 3.8 to 6.6 Hz for 2- and 3-bond coupling. The assignments for C-8 and C-9 are tentative and based on their relative proximity to sulfur.

The correlation of the ^{13}C NMR assignments for the cyclopenta[*d*]pyridazine series (I-III) is shown in Figure 1. The shift ranges for I-IV, respectively, were 31.4, 34.8, 33.8, and 25.7 ppm as compared to 21.7 ppm for azulene. The instability of the compounds, the apparent difficulties in the synthesis of other methyl derivatives of certain structure, and the instrumentation available precluded additional studies.

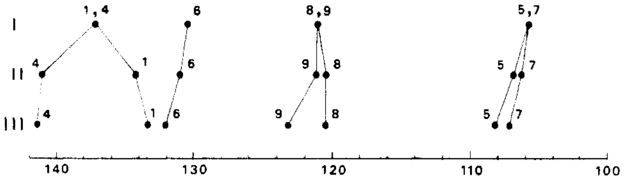

Figure 1. Correlation plot of ^{13}NMR Chemical Shifts (Me_4Si reference) for compounds I-III.

Experimental Section

Compounds. Compounds I-III were prepared as previously described (*7*, *13*).

^{13}C NMR Spectra. Chemical shifts were measured at natural ^{13}C abundance and ambient temperature (ca. 30 °C) with complete proton decoupling on a Varian CFT-20 operating at 20 MHz with the spectrometer in the Fourier-transform mode. A 7-μs pulse width and an acquisition time of 1.023 s were used. The spectrum of I (200 mg), which was not sufficiently soluble in chloroform, was taken in Me_2SO-d_6 (3 mL) and the spectra of II (350 mg) and III (250 mg) were taken in $CDCl_3$ (3 mL) with Me_4Si as the internal reference. The coupled and decoupled spectra of IV (110 mg) were recorded in acetone-d_6 (2.5 mL) with Me_4Si or $(Me_3Si)_2O$ as the internal reference.

The coupling constants for IV (determined from the spectra in acetone-d_6 and the printouts of the maxima in Hz) were as follows: $J_{C_1-H_1} = 161.6$, $J_{C_3-H_3} = 176.6$, $J_{C_3-H_4} = 6.6$, $J_{C_4-H_4} = 162.7$, $J_{C_4-H_3} = 5.0$, $J_{C_6-H_6} = 167.4$, $J_{C_6-H_{5(7)}} = 5.4$, $J_{C_5-H_5} = 182.6$, $J_{C_5-H_6} = 4.2$, $J_{C_4-H_7} = 171.4$, and $J_{C_7-H_6} = 3.8$ Hz.

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