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Synthesis and Properties of N-Cyano Derivatives of Trideca-, Pentadeca-, Heptadeca-, and Nonadecaazafulvenes

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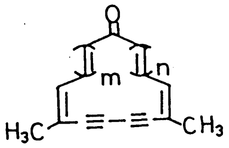
The title azafulvene analogs were synthesized by the reaction of the corresponding annulenones with N,N'-bis(trimethylsilyl)carbodiimide. The ^{1}H NMR spectra reveal that these compounds show larger tropicity than the corresponding dicyanofulvenes and annulenones.

Recently, we have investigated the cyclic cross-conjugated system of ring-expanded fulvenes derived from the bisdehydroannulenones of type 1.[1] Of these, the diphenyl- 2[2a] and dichlorofulvenes 3[2b] proved to be atropic, reflecting the absence of any cross-conjugation of π-electrons, or any contribution from a dipolar structure in the ground state. On the contrary, the dicyanofulvenes 4 proved to show a ring current effect, reflecting some contribution from dipolar structures 4a in the ground state.[3]



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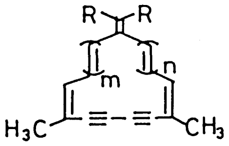
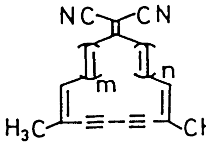


2: R=Ph
3: R=Cl



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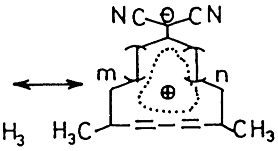
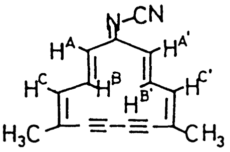


4a



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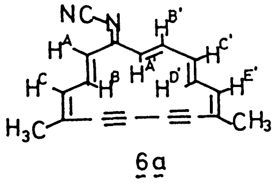
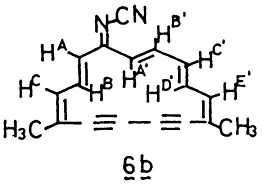
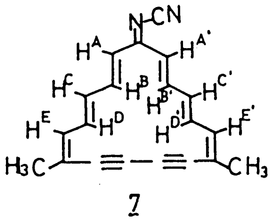


6a



6b



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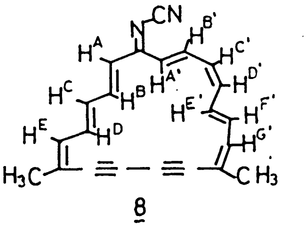

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Table 1. ^1H NMR data of the N-cyanoazafulvenes (δ-values, $CDCl_3$, 500 MHz)

Compd	CH_3	Olefinic protons$^{a)}$
5	1.75 1.74	10.06 (dd, 16.3, 9.9, $H^{B'}$), 10.01 (dd, 16.7, 9.7, H^{B}), 6.38 (d, 16.3, $H^{A'}$), 6.26 (d, 9.9, $H^{C'}$), 6.23 (d, 9.7, H^{C}), 6.17 (d, 16.7, H^{A}).
6a	2.34 2.25	7.81 (dd, 15.3, 5.2, $H^{B'}$), 7.43 (d, 15.7, H^{A}), 7.37 (d, 12.5, $H^{E'}$), 7.35 (d, 11.7, H^{C}), 6.95 (dd, 15.5, 5.2, $H^{C'}$), 5.28 (dd, 15.7, 11.7, H^{B}), 5.07 (d, 15.1, $H^{A'}$), 5.03 (dd, 15.4, 11.8, $H^{D'}$).
6b	2.31 2.24	8.19 (dd, 16.2, 5.3, $H^{B'}$), 7.35 (d, $H^{E'}$), 7.33 (d, H^{C}), 6.98 (dd, $H^{C'}$), 6.92 (d, H^{A}), 5.34 (dd, 16.1, 11.6, H^{B}), 5.05 (dd, $H^{D'}$), 5.00 (d, 16.2, $H^{A'}$).
7	1.79	9.04 (dd, 16.0, 10.5, H^{B}), 9.02 (dd, 15.0, 11.0, H^{D}), 9.00 (dd, 15.0, 11.0, $H^{D'}$), 8.90 (dd, 15.5, 11.0, $H^{B'}$), 6.31 (d, 11.0, $H^{E'}$), 6.28 (d, 11.0, H^{E}), 6.27 (d, 15.5, $H^{A'}$), 6.01 (dd, 15.0, 10.5, H^{C}), 5.99 (dd, 15.0, 10.5, $H^{C'}$), 5.92 (d, 16.0, H^{A}).
8	2.36 2.27	7.73 (dd, 15.4, 6.5, $H^{B'}$), 7.07 (d, 11.3, H^{E}), 6.85 (t, 11.1, $H^{D'}$), 6.75 (dd, 11.1, 6.5, $H^{C'}$), 6.73 (d, 14.9, H^{A}), 6.72 (dd, 15.0, 12.3, H^{C}), 6.62 (d, 8.5, $H^{G'}$), 6.48 (dd, 15.3, 8.5, $H^{F'}$), 6.02 (dd, 15.3, 11.3, $H^{E'}$), 5.82 (dd, 15.0, 11.3, H^{D}), 5.79 (dd, 14.9, 12.3, H^{B}), 5.59 (d, 15.4, $H^{A'}$).

a) In parentheses are the coupling pattern, the coupling constants in Hz and the assignment. In **6b** some of the coupling constants could not be read due to the signal overlap.

In our continuing effort to search two-dimensional push-pull compounds with nonlinear optical behavior,4) we now report the synthesis and properties of the title azafulvenes which bear a strongly electron-withdrawing cyano group at the exocyclic position and are expected to show larger ring current effect than **1** and **4**.

Employing the method of Iwatsuki et al.,5) with N,N'-bis(trimethylsilyl)carbodiimide6) in the presence of titanium tetrachloride in dry benzene at room temperature, [13]annulenone (**1**: m=n=1),1a) [15]annulenone (**1**: m=1, n=2),1b) [17]annulenone (**1**: m=n=2),1b) and [19]annulenone (**1**: m=2, n=3)1b) were converted to the corresponding cyanoimino derivatives.

The cyanoimino[13]annulene **5**7) was obtained as brown needles, mp 184—186 °C, in 55% yield. The ^1H NMR data indicated that **5** has the structure shown with a symmetrical skeleton. The chemical shift assign-

Table 2. The chemical shift differences ($\Delta\delta=\delta_i-\delta_o$) between the inner and outer olefinic protons of annulenones **1**, dicyanofulvenes **4**, and cyanoazafulvenes **5**—**8**,[a)] and the wavelengths (λ_{max}) of the strongest absorption band in THF (in acetonitrile) of the electronic spectra of **5**—**8**

	Δδ/ppm			λ_{max}/nm
	1[b)]	**4**[c)]	**5**—**8**	**5**—**8**
[13]-	3.10	3.48	3.79	291 (289)
[15]-	-1.51	-1.54	-2.21[d)]	327 (325)
[17]-	2.30	2.47	2.72	314 (313)
[19]-	-1.15	——	-1.25[e)]	346 (344)

a) δ_i and δ_o are the average values for the protons β and α positions, respectively, to the methyl group. b) Ref. 2b. c) Ref. 5. d) The value for **6a**. e) The value from the chemical shifts of H^D and H^E.

ments are based on the assumption that the proton close to the cyano group ($H^{A'}$) appears at lower field than H^A. The cyanoimino[15]annulene **6** was obtained as red needles, mp 208—210 °C (dec), in 27% yield. **6** was shown to exist as a mixture of two isomers which have the same skeletal geometry but differ in the orientation of the cyano group, **6a** and **6b**, in a ratio of 7:3. Structures of **6a** and **6b** were assigned by the low-field resonance of the protons close to the cyano group, i. e., H^A in **6a** and $H^{B'}$ in **6b**. The cyanoimino[17]annulene **7** was obtained as brown needles, mp 218—219 °C (dec), in 45% yield. **7** has a symmetrical skeleton as **5**.[8)] The cyanoimino[19]annulene **8** was obtained as dark brown needles, mp 222—223 °C (dec), in 26% yield. The compound was shown to exist as a single isomer with the skeletal geometry shown.[9)]

In compounds **5** and **7** the methyl protons resonate at a high field of about δ 1.75 and the olefinic outer protons appear at higher field than the inner protons, suggesting the paratropic nature of these compounds, in which the macrocyclic moiety would behave as the 12π and 16π system, respectively, due to polarization of the exocyclic bond. On the other hand, in **6** and **8** the methyl protons resonate at a low field of about δ 2.3 and the olefinic outer protons appear at lower field than the inner protons suggesting the diatropicity in these compounds as the 14π and 18π systems.

The chemical shift differences Δδ between the inner and the outer olefinic protons are regarded as an experimental measure of the ring current effect. The values for the cyanoazafulvenes as well as the annulenones and the dicyanofulvenes are listed in Table 2. Among the compounds with the same ring size, the cyanoazafulvene shows the largest $\Delta\delta$ and the annulenone the smallest. This is in accord with a decreasing order of the electron-withdrawing effect of the substituent at the exocyclic position. Thus, albeit having only one cyano group, the cyanoazafulvenes show larger tropicity than **1** and **4**.

As is seen from Table 2, the hypsochromic shifts of the absorption bands in the electronic spectra upon changing the solvent from less polar tetrahydrofuran (THF) to polar acetonitrile, also suggest that the π-electron transfer from the macrocycle to the exocyclic moiety, as depicted in **4a**, occurs in the azafulvenes **5**—**8**.

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References

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7) All azafulvenes gave IR and mass spectra consistent with the assigned structures.
8) Broadening and coalescence of the ^{1}H signals was observed in 70—100 °C region suggesting the syn-anti isomerization of the cyanoimino group on the NMR time scale. The details of the kinetic study will be discussed in a full paper.
9) The coupling constant data of **8** (Table 1) suggest that the macrocyclic ring is rather flexible and presumably nonplanar especially in the tetraene moiety. The orientation of the cyano group was inferred as shown because the chemical shift of H^A (δ 6.73) is close to that in **6b** (δ 6.92) than that in **6a** (δ 7.43). This orientation may be sterically more favorable than the other because of nonplanarity of the tetraene moiety as suggested by rather low H$^{A'}$ (δ 5.59) and high H$^{B'}$ (δ 7.73).

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