

described in Section 3, the results of unpublished experiments^[80], and knowledge of the results of UV irradiation suggest the following possibilities^[136]:

- i) A "direct hit" by the radiation can lead to irreparable breakdown of the nucleic acid molecule.
- ii) The breakdown of one strand of the DNA double strand can in certain circumstances (depending on the nature of the break) be repaired by a mechanism corresponding to enzymatic reactivation.
- iii) The addition of water (*via* H and HO radicals) to the cytosine portion of the DNA leads to a change in the base pairing during the reduplication of the DNA; this could lead *inter alia* to the mutations resulting from ionizing radiation.
- iv) The biological importance of other products [peroxides, dihydrothymine, dihydrouracil, thymine glycols, *etc.* (see Schemes 3 and 4)] formed on irradiation is largely unknown. It is necessary to consider both blockage of the reduplication of the DNA at the modified base and the modification of the genetic

[136] See *W. C. Summers and W. Szybalski, J. molecular Biol.* 26, 227 (1967); *A. Rafi, J. J. Weiss, and C. M. Wheeler, Biochim. biophysica Acta* 169, 230 (1968); *M. Ullrich and U. Hagen, Z. Naturforsch.* 23b, 1176 (1968), as well as [16].

code^[137]. It is not known whether and how the cell is able to recognize and eliminate bases that have been "modified" in this way.

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[137] Cf. [122a].

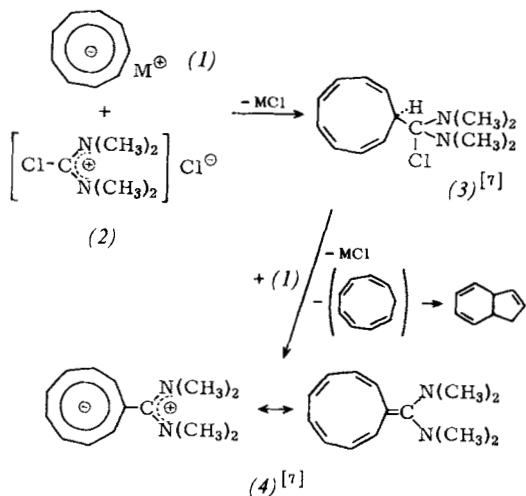
COMMUNICATIONS

10,10-Bis(dimethylamino)nonafulvene^[**]

By *K. Hafner and H. Tappe*^[*]

Dedicated to Professor Cl. Schöpf on the occasion of his 70th birthday

Li-, K- and [(CH₃)₄N] cyclononatetraenides (1)^[1] are the only monocyclic derivatives of the hypothetical cyclononatetraene that have been isolated so far^[2]. Nonafulvenes, being cross-conjugated 10 π electron systems and homologs of the fulvenes, are of particular interest. Like the fulvene and isobenzofulvene systems^[3], nonafulvenes should also be stabilized by electron-donating substituents on the exocyclic C-atom. The successful synthesis of 10,10-bis(dimethylamino)nonafulvene (4) confirms this presumption.



Compound (1), M = Li, reacts with *N,N,N',N'*-tetramethylchloroformamidinium chloride (2)^[4] at -70°C in tetrahydrofuran to give the so far non-isolable cyclononatetraene derivative (3), which, in the presence of an excess of (1), is rapidly converted into the nonafulvene (4) as yellow crystals that are sensitive to light and air [yield 7%; m.p. $109-110^{\circ}\text{C}$ (from ethanol)]^[5]. In addition, 3a,7a-dihydroindene^[6] is formed as a result of protonation of (1) and subsequent valence isomerization of the cyclononatetraene thus formed. Elemental analysis and molecular weight determination confirm the constitution of (4); its configuration, however, has not yet been elucidated^[7]. During quantitative microhydrogenation, compound (4) takes up H₂ in amounts calculated for five double bonds. The mass spectrum of (4) shows several, but uncharacteristic, fragmentation peaks in addition to the molecular peak $m/e = 216$.

UV and NMR spectra of (4) indicate the presence of a temperature- and solvent-dependent conformational equilibrium. In *n*-hexane at room temperature, compound (4) absorbs at 330 nm ($\log \epsilon = 4.34$), whereas in methylene chloride it absorbs at 403 (3.90), 340 (4.05), 298 (4.05), and 244 (4.28) nm ($\log \epsilon$), and in tetrahydrofuran at 334 (4.19) and at 240 (4.15) nm ($\log \epsilon$). Although the UV spectrum of (4) in *n*-hexane remains unchanged at low temperatures, in methylene chloride the extinction of the bands at 403, 296, and 244 increases whereas the absorption maximum of the band at 340 decreases; at -80°C that at 340 disappears. [λ_{max} at 0°C : 403 (3.9), 340 (4.0), 296 (4.1), 244 (4.3); at -35°C : 403 (3.9), 296 (4.2), 244 (4.4); at -80°C ^[7a]: 403 (4.1), 294 (4.4), 244 (4.7) nm ($\log \epsilon$)]. In tetrahydrofuran at temperatures below 0°C , two additional maxima appear at 404 and 296 nm whose intensities increase on lowering the temperature [λ_{max} at -35°C ^[7a]: 404 (3.8), 335 (4.1), 296 (4.1), 244 (4.4); at -80°C : 404 (4.1), 335 (4.0), 296 (4.3), 244 (4.6) nm ($\log \epsilon$)]. The NMR spectrum of (4) (in CD₂Cl₂) (Fig. 1) at 35°C shows a sharp singlet at $\tau = 7.22$ for the twelve methyl

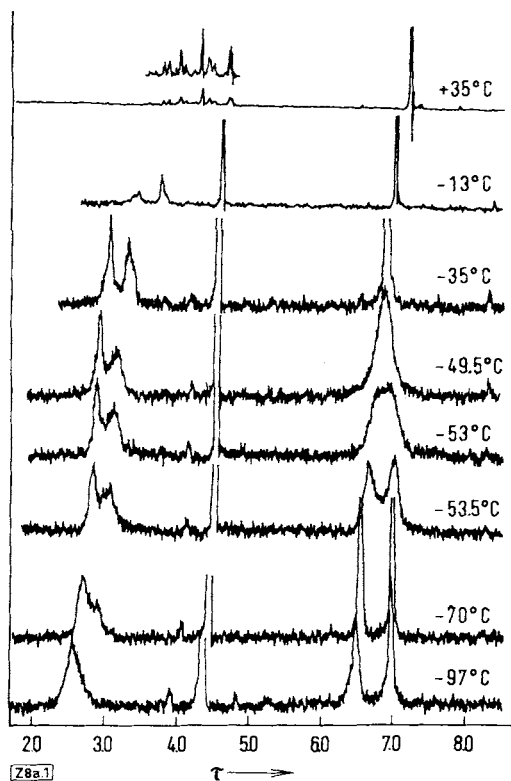
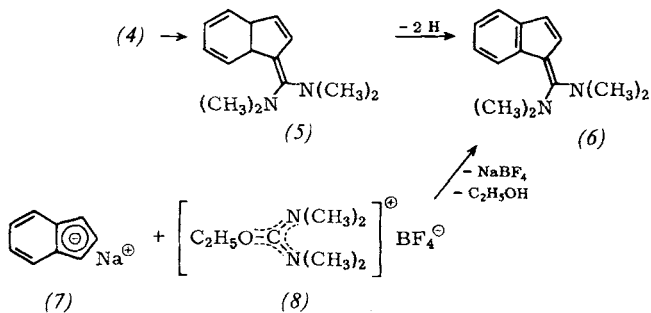


Fig. 1. NMR spectra of 10,10-bis(dimethylamino)nonafulvene (4) at various temperatures in CD_2Cl_2 (60MHz; tetramethylsilane as internal standard).

protons, in addition to a complicated multiplet between $\tau = 3.63$ and 4.67 for the eight ring protons. At lower temperatures the multiplet of the ring protons is shifted to lower field with diminution of the fine structure, while the singlet of the methyl protons is split into a doublet (coalescence point: ca. -53°C). This may be ascribed to either restricted rotation of the C-N bonds or formation of an unsymmetrical conformation of the nine-membered ring relative to the dimethylamino groups at low temperatures^[8]. The temperature-dependent changes in the NMR and UV spectra of (4) are reversible.



As a derivative of the hypothetical cyclononatetraene, compound (4) undergoes an irreversible thermal valence isomerization in benzene, slowly at room temperature but rapidly at 60°C , to give the 3a,7a-dihydroindene derivative (5) [yield 50%; yellow oil, sensitive to oxygen; b.p. $80^\circ\text{C}/0.003$ torr; UV spectrum (in *n*-hexane): 302 (4.17), 270 (4.12), 260 (4.06) nm (log ϵ); NMR spectrum (in CDCl_3): doublet centered at $\tau = 7.34$ (4 CH_3), multiplets centered at $\tau = 6.17$ (H-3a, H-7a), at 4.55 (H-2, H-3, H-4, H-5, H-6), and at 3.65 (H-7)]. The NMR spectrum of (5) does not provide sufficient data for a differentiation between the *cis* and *trans* isomer. Oxidation of (5) with active lead dioxide^[9] leads to the formation of 6,6-bis(dimethylamino)benzo[*b*]fulvene [1-(tetramethyldiaminomethylene)indene] (6), which can also be prepared

from sodium indenide (7) and bis(dimethylamino)ethoxy-carbonium fluoroborate (8)^[10] [yellow crystals, sensitive to light, m.p. 55°C ; UV spectrum (in *n*-hexane): 375 (4.36), 279 (4.08), 255 (3.96) nm (log ϵ); NMR spectrum (in CDCl_3): singlet at $\tau = 6.99$ (4 CH_3), AB system at $\tau = 3.32$ and 3.42 (2H) ($J_{\text{AB}} = 5$ Hz), multiplet centered at $\tau = 2.75$ (4 benzenoid H)].

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[1] T. J. Katz and P. J. Garrat, *J. Amer. chem. Soc.* 86, 5194 (1964); E. A. LaLancette and R. E. Benson, *ibid.* 87, 1941 (1965); H. E. Simmons, D. B. Chesnut, and E. A. LaLancette, *ibid.* 87, 982 (1965).

[2] D. Lloyd and N. W. Preston, *Chem. and Ind.* 1966, 1039, reported on the synthesis of diazocyclononatetraene but the product could not be obtained in an analytically pure state; proof of structure was based on IR spectroscopic findings alone. The structure of the cyclononatetraene-M(CO)₃ complexes (M = Mo, W, Cr) prepared by R. B. King and F. G. Stone, *J. Amer. chem. Soc.* 82, 4557 (1960), was, as far as we know, not unequivocally proved.

[3] K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H. Vöpel, *Angew. Chem.* 75, 35 (1963); *Angew. Chem. internat. Edit.* 2, 123 (1963); K. Hafner, K. H. Vöpel, G. Ploss, and C. König, *Liebigs Ann. Chem.* 661, 52 (1963); K. Hafner, G. Schulz, and K. Wagner, *ibid.* 678, 39 (1964); K. Hafner and W. Bauer, *Angew. Chem.* 80, 312 (1968); *Angew. Chem. internat. Edit.* 7, 297 (1968).

[4] H. Eilingsfeld, G. Neubauer, M. Seefelder, and H. Weidinger, *Chem. Ber.* 97, 1232 (1964).

[5] Correct analytical results were obtained for all the products described.

[6] St. W. Staley and T. J. Henry, *J. Amer. chem. Soc.* 91, 1239 (1969); P. Radlick and W. Fenical, *ibid.* 91, 1560 (1969); further literature cited therein.

[7] The all *cis*-configuration given in the scheme for (3) and (4) is arbitrary.

[7a] The average error of the extinction coefficients in the low-temperature spectra is about ± 5 –10%.

[8] We thank Dr. D. Jung for recording and discussing the NMR spectra.

[9] R. Kuhn and J. Hammer, *Chem. Ber.* 83, 413 (1950).

[10] H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Liebigs Ann. Chem.* 641, 1 (1961).

cis,cis,cis,cis-1,3,5,7-Cyclononatetraene

By G. Boche, H. Böhme, and D. Martens^[*]

Cyclononatetraenes possibly occur as intermediates in the thermal and in the photochemical valence isomerization of *cis*-bicyclo[6.1.0]nona-2,4,6-triene or various 9- and 9,9'-substituted *cis*-bicyclo[6.1.0]nona-2,4,6-trienes into *cis*- and *trans*-bicyclo[4.3.0]nona-2,4,7-trienes (*cis*- and *trans*-dihydroindenenes)^[1]. Furthermore, *cis,cis,cis,cis*-1,3,5,7-cyclononatetraene^[1g] (2) and 9-methyl-*cis,cis,cis,cis*-1,3,5,7-cyclononatetraene^[1k] are assumed to occur as non-isolable primary products in the protonation and methylation of the cyclononatetraenyl anion (1). King and Stone^[2] have reported that the tricarbonylmetal complexes obtained in small yield by reaction of dihydroindene with $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ probably contain *cis,trans,cis,trans*-1,3,5,7-cyclononatetraene as olefinic ligand.

