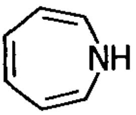
4,9-METHANO-1*H*-AZA[11]ANNULENE : A 12π-HOMOLOGUE OF PYRROLE[#]

Walter Lange, Wilhelm Haas, Hans Schmickler, and Emanuel Vogel*

Institut für Organische Chemie der Universität zu Köln, Greinstraße 4,
D-5000 Köln 41, Federal Republic of Germany

Abstract – 4,9-Methano-1*H*-aza[11]annulene (3), to be regarded as a 12π-homologue of pyrrole, was synthesized from 1,6-methano[10]annulene by a reaction sequence patterned after that employed in the conversion of benzene to 1*H*-azepine (1). In contrast to 1, which is atropic, 3 - a bridged structural variant of the elusive 1*H*-aza[11]annulene - qualifies as paratropic, although its peripheral eleven-membered ring possesses a non-planar conformation.

The homologues of the π-excessive pyrrole, subdivided into 1*H*-aza[4n+1]annulenes and 1*H*-aza[4n-1]annulenes containing 4n+2 and 4n π-electrons,[1] respectively, rank among the more important heterocycles whose development has been spurred by Hückel's famous rule. While the potentially aromatic 1*H*-aza[4n+1]annulenes with n>1 have yielded to synthesis up to 1*H*-aza[17]annulene[2] and were found to be diatropic even when deviating from planarity to some extent,[3] 1*H*-aza[4n-1]annulenes sufficiently flattened out as to form an anti-aromatic 4n π-electron configuration - and hence to sustain a paramagnetic ring current - have remained chemical rarities.[4] *1H-Azepine (1),*[5] *the only pyrrole homologue of the 4n π type known in parent form, possesses a markedly non-planar* conformation (boat-shaped) which causes the molecule to be atropic.[6]



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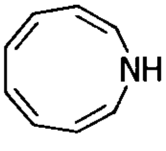

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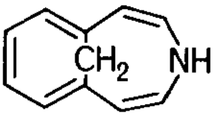

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In order to corroborate the notion that pyrrole type heteroannulenes correspond to carbocyclic annulenes in showing an alternation of the electromagnetic properties,[7] the synthesis of a 1*H*-aza[11]annulene that could be looked upon as the next higher homologue of the strongly diatropic 1*H*-aza[9]annulene (2)[1b, 2a,b] was deemed to be very desirable. As the parent 1*H*-aza[11]annulene suffers from severe geometric constraints that do not allow for meaningful comparisons, our interest focused on its bridged variant, the 4,9-methano-1*H*-aza[11]annulene (3).[8]

The conceptually most obvious approach to 3 is the pathway which starts out from 1,6-methano[10]annulene (4) and follows the pattern of synthesis of 1 via benzene and N-methoxycarbonyl-1*H*-azepine.[5] Realization of this scheme crucially depended on the course of reaction of 4 with methyl azidoformate. As it turned out, addition of methoxycarbonylnitrene (generated thermally from the azide) to 4 occurred with comparable rates at the 1,2-, 2,3-, and 3,4-bonds, affording as the isolated products compounds **8**, **9**, and **10**, respectively, although MO-calculations suggest the 1,2- and 2,3-bonds to be the sites of preferred electrophilic attack. That the aziridine intermediates **5** and **7** would readily undergo a thermally-allowed 10π-electrocyclic rearrangement to give the respective

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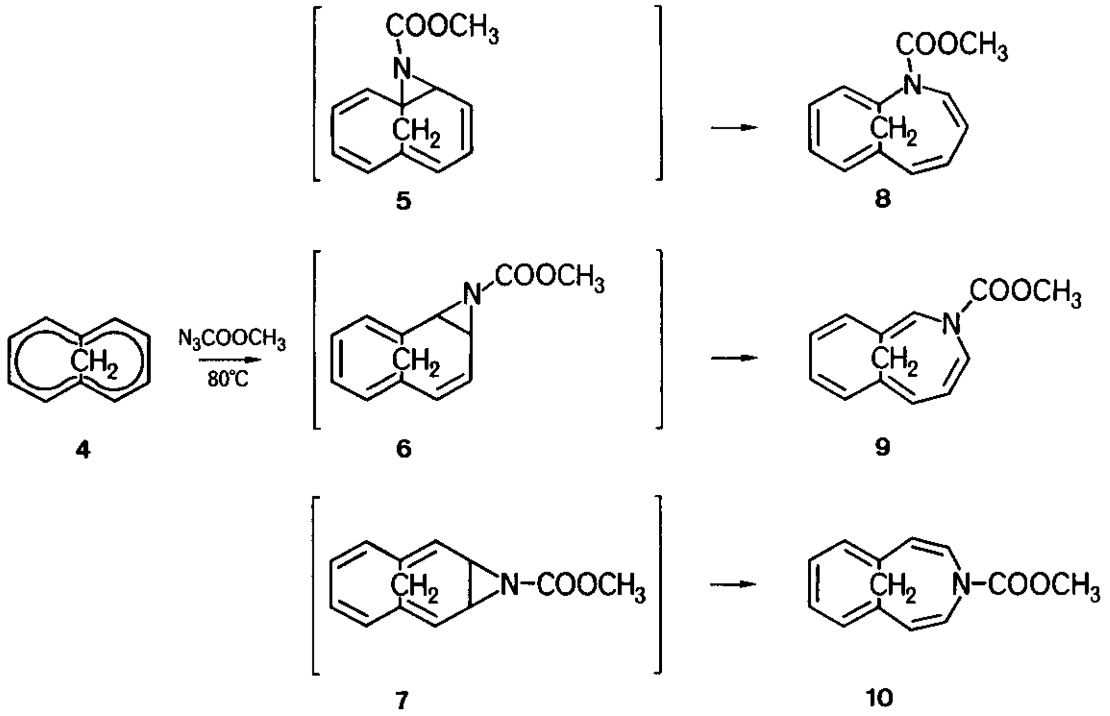
[#] *Dedicated to Professor Sir Derek Barton on the occasion of his 70th birthday* methanoaza[11]annulenes (**8** and **10**) was anticipated for thermodynamic reasons since these products contain energetically favourable cycloheptatriene structural units. In the case of the aziridine **6** where the product lacks such a unit, the occurrence of the rearrangement was not readily predictable.[9] Isolation of the methanoaza[11]annulenes **8**, **9**, and **10** was achieved best when the conditions employed in the nitrene addition to **4** were as follows:

10.1 g (0.1 mol) of methyl azidoformate and 28.4 g (0.2 mol) of **4** were heated without solvent to 80°C for four days (argon atmosphere) whereupon the reaction was halted in order to avoid excessive decomposition of the products and to minimize the formation of bis-adducts. After removal of unreacted azide by distillation (in vacuo) and recovery of residual **4** by putting the reaction mixture on top of a short aluminum oxide column and eluting the hydrocarbon with pentane, the products were chromatographed on a 100 x 4 cm aluminum oxide column with ether-pentane (1:4) to give three fractions containing **8**, **9**, and **10** (in that order), respectively: **8**, mp 52-53°C, orange cubes (pentane), 0.66 g (10 %, based on reacted **4**); **9**, mp 67-68°C, red needles (pentane), 0.72 g (11 %); **10**, mp 120-121°C, yellow plates (pentane), 0.41 g (6 %).



The ^1H nmr spectrum of **10** at room temperature shows an absorption pattern (AA'BB'-system and AB-system for the vinylic protons, AX-system for the bridge protons, and singlet for the methyl protons) and coupling constants fully consistent with a N-methoxycarbonyl-4,9-methano-1*H*-aza[11]annulene of C_s-symmetry (Figure 1a and Table 1). As the temperature is lowered to -20°C, the AB-system of H-2,3 is transformed into two partially overlapping AB-systems, whereas the other resonances remain essentially unaffected. This temperature dependence of the spectrum can hardly be explained other than by assuming that on cooling the rotation of the $COOCH_3$ group around the N-CO axis becomes slow on the nmr time scale. The same conclusion regarding the dynamic behaviour of **10** is reached on an inspection of the ^{13}C nmr spectrum of the compound. The relatively large difference in the chemical shifts of the bridge protons (3.6 ppm), with Ⓗ-12 resonating at exceptionally low field, is indicative of the syn-arrangement of the heteroatom with respect to the bridge, a conformational preference that appears to be

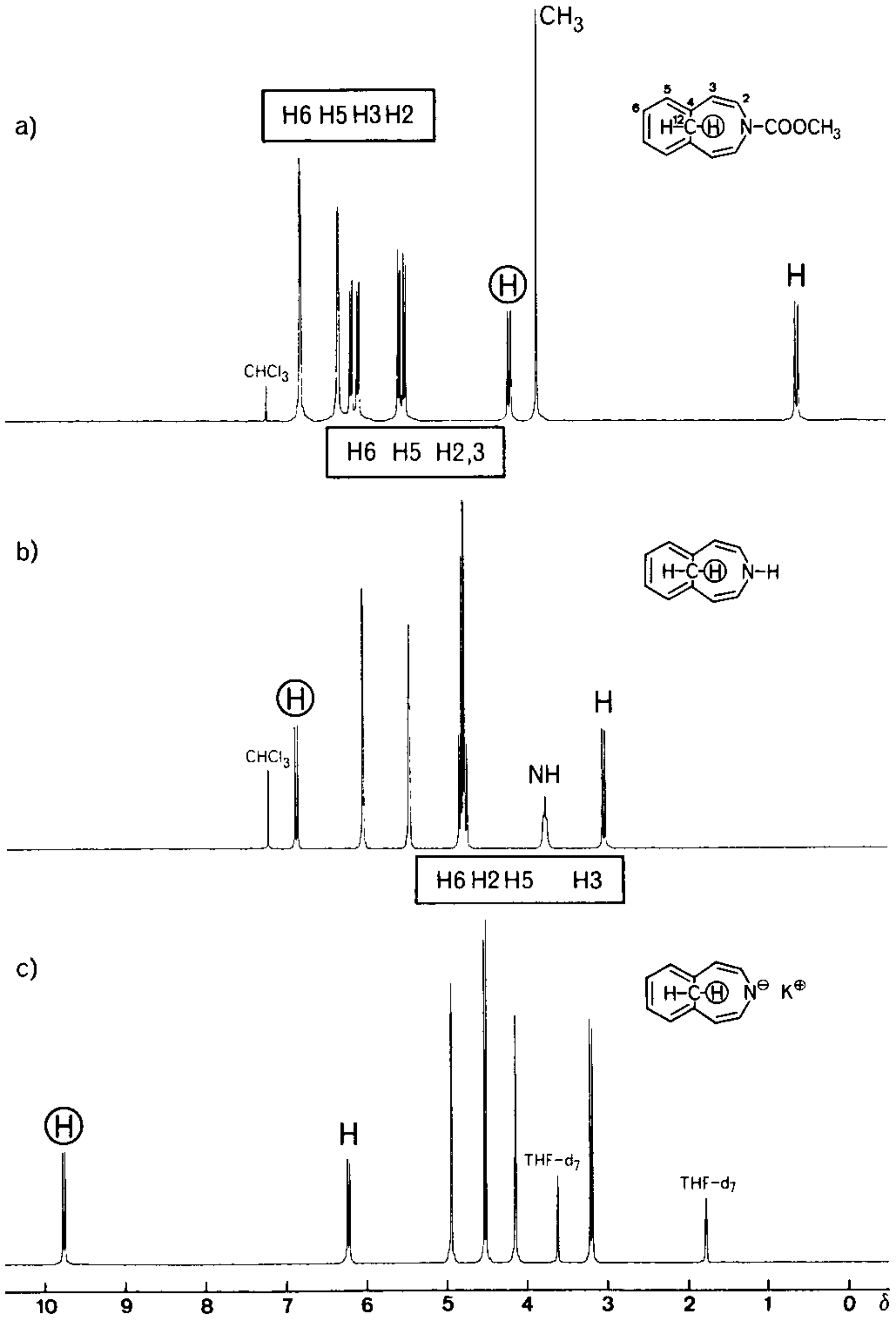


Figure 1. ^{1}H Nmr spectra (300 MHz) of a) N-methoxycarbonyl-4,9-methano-1*H*-aza[11]annulene (**10**) ($CDCl_3$, -20°C), b) 4,9-methano-1*H*-aza[11]annulene (**3**) ($CDCl_3$, -20°C), and c) 4,9-methano-1*H*-aza[11]annulenyl anion (**11**) (THF-d_8, -10°C)

general for 4,9-methano-hetero[11]annulenes.[8] Significantly, the chemical shifts of the vinylic protons of **10** agree remarkably well with those of the corresponding protons of the parent hydrocarbon, bicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene (**12**)[8] (Table 1), if one allows for the effect of nitrogen on the shifts of H-2,3, and hence convincingly prove **10** to be devoid of a paramagnetic ring current.

An X-ray crystallographic analysis of **10** (Figure 2)[10] not only indicates the presence of an olefinic heteroannulene, the array of localized double bonds linked by a mildly pyramidal ring nitrogen, but also reveals that the syn-conformation presumed to be true for the molecule in solution definitely applies to its solid state.

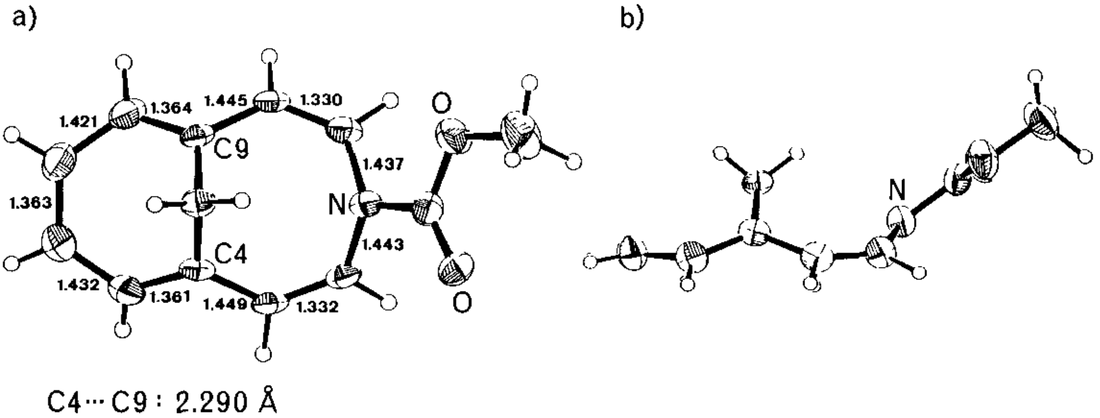
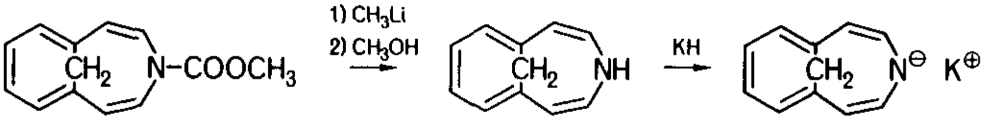


Figure 2. Molecular structure of N-methoxycarbonyl-4,9-methano-1*H*-aza[11]annulene (**10**): a) top view; b) side view.

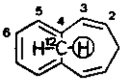
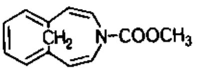
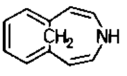
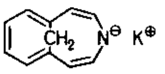
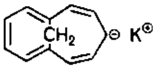
Conversion of **10** into 4,9-methano-1*H*-aza[11]annulene (**3**) was smoothly effected by means of methyllithium. In a typical run 0.22 g (1 mmol) of **10** in 100 ml of THF were treated with five equivalents of ethereal methyllithium (-20°C, 1 h) and the deep blue solution of the anion of **3** thus formed quenched by methanol at -20°C. After conventional work-up, the product was distilled in high vacuum (10^{-5} torr, 20°C) furnishing **3** as a red liquid that solidified on a cold finger (-70°C); 70 mg (45 %). By analogy to **1**, compound **3** is very unstable, polymerizing rapidly even when air is excluded.



10 **3** **11**

The ^{1}H nmr spectrum of **3** (Figure 1b and Table 1), while retaining the same pattern as that of **10** as far as the vinylic and bridge proton resonances are concerned (except for the merging of the signals of H-2 and H-3), exhibits a new signal broadened by coupling (δ 3.74) that arises from the NH-proton. The important feature of the spectrum relevant to this study is that the absorption centroid of the vinylic protons ($\bar{\delta}_v$) has moved upfield quite markedly (0.9 ppm), whereas that of the bridge protons ($\bar{\delta}_b$) has experienced an even more pronounced downfield shift (2.6 ppm). Evidently, **3** is capable of sustaining a sizeable paramagnetic ring current. As **1** is atropic, and as there are strong indications - such as the virtual invariance of the shift difference $\delta_{\textcircled{H}\text{-}12} - \delta_{H\text{-}12}$ in **10**, **3**, and **11** - that **3** possesses a non-planar aza[11]annulene ring similar in conformation to that of **10**, paratropicity of **3** is noteworthy.

Table 1. ^{1}H Nmr chemical shifts (in ppm) and ^{1}H,^{1}H-coupling constants (in Hz) of **3**, **10**, **11**, **12**, and **13**.

	H-2	H-3	H-5	H-6	$\bar{\delta}_v$	H-12	Ⓗ-12	$\bar{\delta}_b$
 **12**	4.78	6.28	6.29	6.74	6.02	0.21	3.72	1.97
	$^3J_{2,3}$ = 11.48		$^3J_{5,6}$ = 6.02	$^3J_{6,7}$ = 10.58		$^2J_{12,12}$ = 11.57		
 **10**	5.54*	6.12*	6.32	6.80	6.20	0.60	4.19	2.40
	$^3J_{2,3}$ = 8.38		$^3J_{5,6}$ = 5.55	$^3J_{6,7}$ = 10.58		$^2J_{12,12}$ = 11.01		
 **3**	4.81	4.76	5.47	6 05	5.27	3.02	6 88	4.95
	$^3J_{2,3}$ = 9.59		$^3J_{5,6}$ = 5.32	$^3J_{6,7}$ = 10.55		$^2J_{12,12}$ = 10.53		
 **11**	4.51	3.18	4.12	4.91	4.18	6.18	9.70	7.94
	$^3J_{2,3}$ = 9.24		$^3J_{5,6}$ = 4.65	$^3J_{6,7}$ = 10.16		$^2J_{12,12}$ = 8.83		
 **13**	2.99	2.31	3.16	3.92	2.89	10.31	14.19	12.25
	$^3J_{2,3}$ = 10.4		$^3J_{5,6}$ = 4.7	$^3J_{6,7}$ = 9.0		$^2J_{12,12}$ = 9.6		

*average of two AX-systems (hindered rotation around the N-CO bond)

Table 2. Spectroscopic data of **3**, **10**, and **11**.

10: ^{1}H nmr: see Figure 1 and Table 1; ^{13}C nmr (75.5 MHz, $CDCl_3$): δ 155.8, 129.7, 124.4, 124.1, 117.6, 117.4, 53.4, 29.6; ir (KBr): $\tilde{\nu}$ = 3026, 2953, 1724, 1626, 1615, 1561 cm^{-1}; uv/vis (dioxane): λ_{max} = 263 nm (ε = 47000), 333 (1620); ms (70 eV): m/z 215 (M^+, 30 %), 156 (36), 128 (100).

3: ^{1}H nmr: see Figure 1 and Table 1; ^{13}C nmr (75.5 MHz, $CDCl_3$): δ 130.8, 125.8, 125.2, 118.9, 110.8, 36.4; ir (CCl_4): $\tilde{\nu}$ = 3441, 3404, 3030, 2935, 2880, 1652, 1636 cm^{-1}; uv/vis (cyclohexane): $\lambda_{max,1}$ = 257 nm, $\lambda_{max,2}$ = 403 nm ($\varepsilon_1/\varepsilon_2$ = ca. 82/1*); ms (70 eV): m/z 157 (M^+, 60 %), 156 (97), 130 (100).

11: ^{1}H nmr: see Figure 1 and Table 1; ^{13}C nmr (75.5 MHz, THF-d_8, -30°C): δ 146.0, 144.9, 131.9, 111.6, 104.1, 50.9.

*the extreme air sensitivity of **3** precluded quantitative measurement of the extinction coefficients

4,9-Methano-1*H*-aza[11]annulene (**3**) on treatment with potassium hydride (THF-d_8, -78°C) affords an anion readily identified by its ^{1}H and ^{13}C nmr spectra as **11**. As shown in Figures 1b and 1c, formation of **11** gives rise to a ^{1}H nmr spectrum in which the absorption centroids of the vinylic and bridge protons have undergone an additional pronounced upfield (1.1 ppm) and downfield (3.0 ppm) shift, respectively. While these changes can be explained in terms of enhanced paratropism in **11**, the possibility that part of the upfield shift of the vinylic proton resonances is due to shielding by the negative charge must be considered. The emergence of paratropism on conversion of **10** to **3** and its marked increase on formation of **11** may be inferred independently from the ^{13}C nmr spectra on the basis of the deshielding observed for the bridge carbon as one goes from **10** to **11** ($\delta_{C\text{-}12}$: 29.6 $\rightarrow$ 36.4 $\rightarrow$ 50.9).[11,12] In conclusion it should be noted that the paratropicity of **11** is distinctly less than that of the bicyclo[5.4.1]dodecapentaenyl anion (**13**),[13] isoelectronic to **11**, for the obvious reason that the electronegativity of nitrogen does not allow the negative charge to be involved in anti-aromatic delocalization as effectively as in the carbanion.

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7. Such an alternation has been shown by P. J. Beeby and F. Sondheimer [*Angew. Chem.*, 1973, **85**, 406; *Angew. Chem. Int. Ed. Engl.*, 1973, **12**, 411] to exist in the N-ethoxycarbonyl derivatives of a series of rigidly flat 1*H*-azaannulenes with 18, 20, and 22 π-electrons, respectively.
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10. Crystal data : **10** crystallized from pentane in the monoclinic space group $P2_1$, with a = 12.509(2) Å, b = 4.514(1) Å, c = 10.309(2) Å, β = 107.30(2)°, Z = 2, d_c $(g \cdot cm^{-3})$ = 1.286; R = 0.058, number of unique reflections: 2123.
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