Structural Studies of *syn*-1,6:8,13-Diimino[14]annulenes. 2. Molecules with Connected Bridges

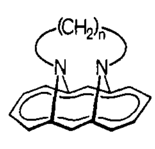
Riccardo Destro,† Tullio Pilati,† Massimo Simonetta,*† and Emanuel Vogel‡

Contribution from the Dipartimento di Chimica Fisica ed Elettrochimica, e Centro CNR, Università, Via Golgi 19, Milano, and the Institut für Organische Chemie der Universität, Greinstrasse 4, D-5000 Köln 41, West Germany. *Received August 3, 1984*

Abstract: The crystal structures of 1,6:8,13-diiminomethano[14]annulene (**5**), 1,6:8,13-diiminoethano[14]annulene (**6**), and 1,6:8,13-diiminopropano[14]annulene (**7**) have been determined by X-ray diffraction at room temperature. The geometries of the three molecules and those of the corresponding hydrocarbons 1,6:8,13-propane-1,3-diylidene[14]annulene (**5a**), 1,6:8,13-butane-1,4-diylidene[14]annulene (**6a**), and 1,6:8,13-pentane-1,5-diylidene[14]annulene (**7a**) have been compared. It appears that, in contrast with what was observed for the hydrocarbons, the strain imposed on the ring does not increase significantly with the increase of the number of carbon atoms connecting the two nitrogen atoms. As a consequence, the distortion of the annulene ring on going from **5** to **7** is increased to a much lesser extent than that found in the **5a**-**7a** series. A noticeable difference between the two series is also shown by the values of the dihedral angles between the planes of the two bridges. All these observations find a rationale in the softness of the nitrogen atom in comparison with the stiffness of the methine group.

In a previous paper[1] we have described the structural features of *syn*-1,6:8,13-diimino[14]annulene (**1**) and three of its derivatives, *syn*-1,6-(methylimino)-8,13-imino[14]annulene (**2**), *syn*-1,6:8,13-bis(methylimino)[14]annulene (**3**), and the perchlorate salt of **1** (**4**). These molecules showed a variety of interactions between the bridging groups, such as intramolecular hydrogen bonds in **1** and **2**, pure repulsion between the two $>NCH_3$ groups in **3**, and strong electrostatic attraction between a proton and the nitrogen atoms in **4**. The influence of these different interactions on the geometry of the annulene system was examined, and a discussion was also given on the possible occurrence, even in the solid state, of the configurational conversion of the two nitrogen atoms of **1**, a dynamic process that certainly takes place in solution.[2]

We now present the results of an X-ray investigation on three other derivatives of **1**, where the nitrogen atoms of the bridges are connected by $-CH_2-$ groups, according to the general structural formula



syn
aromatic

For the molecules here described, **5** (n = 1), **6** (n = 2), and **7** (n = 3), it was of particular interest to verify if the strain imposed on the anthracene skeleton by an increasing number of methylene groups in the bridges resulted in the same dramatic increase of deformation of the annulene ring as shown by the corresponding hydrocarbons (**5a**, **6a**, and **7a**, respectively) which had previously been studied in our laboratories.[3-5] The substitution of methine groups with nitrogen atoms at the extrema of the chain forming the bridge was expected to cause a modification of the geometry of these systems, particularly at the bridgehead sites, but the extent of difference between the two series of compounds could obviously be determined only by comparison of the corresponding molecular dimensions, as reported in this work.

Experimental Section

All data were collected on an Enraf-Nonius CAD-4 diffractometer, equipped with graphite monochromator and using Mo Kα radiation (λ = 0.7107 Å). Unit-cell dimensions (Table I) were obtained from the setting angles of medium-angle (2θ between 22° and 42°) reflections centered before and after each set of intensity measurements. Details of data collection and analysis are given in Table II.

The structure of **5** was solved by direct methods (MULTAN),[7] while for **6** an initial model was derived from the atomic parameters of **6a**,[4b] crystal data having suggested isomorphism of the two substances. Since no solution could be obtained by conventional application of direct methods to **7**, the constrained least-squares method recently devised by the Milano group[8] was applied. Hydrocarbon **7a** was assumed as the starting molecular model, and the structure was easily solved in the first application of the procedure.

Preliminary positions of the hydrogen atoms in all three structures were derived from difference maps calculated during the course of the refinement.[9] In the final full-matrix least-squares cycles, the sets of

Table I. Crystal Data

	compound		
	5	6	7
formula	$C_{15}H_{12}N_2$	$C_{16}H_{14}N_2$	$C_{17}H_{16}N_2$
fw	202.3	234.3	248.3
system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$Fmm2$	$C2$
a, Å	8.685 (1)	17.391 (3)	17.407 (2)
b, Å	6.687 (2)	11.561 (3)	6.310 (1)
c, Å	18.985 (4)	5.995 (1)	11.975 (2)
β, deg	95.67 (1)		93.13 (1)
V, Å^3	1097.2 (7)	1207.4 (7)	1313.4 (6)
Z	4	4	4
ρ_{obsd}, g cm^{-3} (flotation)	1.32	1.28	1.25
ρ_{calcd}, g cm^{-3}	1.333	1.289	1.256
$F(000)$	464	496	528
μ(Mo Kα), cm^{-1}	0.74	0.72	0.69

(1) Destro, R.; Pilati, T.; Simonetta, M.; Vogel, E. *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) Vogel, E.; Kuebart, F.; Marco, J. A.; Andree, R. *J. Am. Chem. Soc.* **1983**, *105*, 6982-6983.
(3) For **5a**: (a) Vogel, E.; Vogel, A.; Kübbeler, H. K.; Sturm, W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 514-516. (b) Gavezzotti, A.; Mugnoli, A.; Raimondi, M.; Simonetta, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 425-431.
(4) For **6a**: (a) Vogel, E.; Sturm, W.; Cremer, H. D. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 516-517. (b) Gramaccioli, C. M.; Mugnoli, A.; Pilati, T.; Raimondi, M.; Simonetta, M. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2365-2370.
(5) For **7a**: Bianchi, R.; Mugnoli, A.; Simonetta, M. *Acta Crystallogr., Sect. B*, **1975**, *B31*, 1283-1287.
(6) Cromer, D. T.; Weber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2.B and 2.2.C, pp 99-102.
(7) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368-376.
(8) Bianchi, R.; Gramaccioli, C. M.; Pilati, T.; Simonetta, M. *Acta Crystallogr.*, , *Sect. A* **1981**, *A37*, 65-71.
(9) Programs used for data collection, least-squares refinement, and calculation of molecular dimensions are those quoted in ref 1.

†Dipartimento di Chimica Fisica ed Elettrochimica, e Centro CNR, Università.
‡Institut für Organische Chemie der Universität.

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Table II. Details of Data Collection and Refinement

	compound		
	5	**6**	**7**
cryst dimensions, mm	0.28 × 0.125 × 0.075	0.30 × 0.24 × 0.18	0.30 × 0.28 × 0.20
technique of data collectn[a] (ω scan)			
scan rate, deg/min	1.3–10	1.0–10	1.5–10
scan width, deg	0.9 + 0.347 tan θ	0.9 + 0.347 tan θ	1.0 + 0.347 tan θ
max 2θ angle, deg	50	60	55
reflcns and std dev[b]			
no. of reflcns measd	1908	516	1672
no. of indep reflcns	1908	516	1391
N = no. of reflcns with net counts above bkgd ($I > 0$)	1618	475	1269
N_1 = no. of reflcns with $I > 2\sigma(I)$	1111	383	960
assumed std dev (σ_c from counting statistics)	$\sigma = [\sigma_c^2 + (0.03I)^2]^{1/2}$	$\sigma = [\sigma_c^2 + (0.03I)^2]^{1/2}$	$\sigma = [\sigma_c^2 + (0.03I)^2]^{1/2}$
least-squares refinement[c]			
no. of observtns (m)	1618	475	1269
no. of refined parameters (p)	203	61	236
g (isotropic ext coeff) × 10^6	9 (2)	10 (2)	7 (1)
$R(F) = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$			
on N	0.086	0.052	0.058
on N_1	0.051	0.041	0.042
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum w F_o^2]^{1/2}$	0.054	0.042	0.044
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m-p)]^{1/2}$	1.16	1.35	1.31
convergence, largest shift	0.05σ	0.08σ	0.12σ
high peak in final diff map, e Å^{-3}	0.26	0.17	0.24

[a] Mo Kα radiation, λ = 0.7107 Å; graphite monochromator. No variations, other than those expected from counting statistics, were shown by three standard reflections frequently monitored during data collection. [b] Data were corrected for Lorentz and polarization effects but not for absorption. [c] The quantity minimized was $\sum w(\lvert F_o\rvert - k'\lvert F_c\rvert)^2$, with weights $w = 4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors were from ref 6.

Table III. Atomic Parameters for **5**

atom	x	y	z	U_{iso}
C(1)	0.2993 (3)	0.4317 (4)	0.3969 (2)	0.0456 (11)
C(2)	0.1659 (4)	0.4128 (6)	0.4317 (2)	0.0574 (13)
C(3)	0.1408 (4)	0.2648 (6)	0.4799 (2)	0.0631 (15)
C(4)	0.2156 (4)	0.0804 (6)	0.4878 (2)	0.0596 (14)
C(5)	0.3269 (4)	0.0060 (6)	0.4485 (2)	0.0520 (13)
C(6)	0.4207 (3)	0.1228 (4)	0.4096 (1)	0.0416 (10)
C(7)	0.4962 (4)	0.0582 (5)	0.3524 (2)	0.0449 (11)
C(8)	0.5593 (3)	0.1925 (4)	0.3075 (1)	0.0406 (10)
C(9)	0.6086 (4)	0.1468 (6)	0.2415 (2)	0.0538 (13)
C(10)	0.6182 (4)	0.2830 (6)	0.1873 (2)	0.0594 (14)
C(11)	0.5419 (4)	0.4675 (7)	0.1793 (2)	0.0656 (15)
C(12)	0.4455 (4)	0.5531 (5)	0.2234 (2)	0.0594 (14)
C(13)	0.4373 (3)	0.5003 (4)	0.2945 (2)	0.0445 (11)
C(14)	0.3117 (4)	0.5295 (5)	0.3328 (2)	0.0500 (12)
C(15)	0.5730 (4)	0.4150 (6)	0.4049 (2)	0.0462 (12)
N(1)	0.4342 (3)	0.3305 (3)	0.4299 (1)	0.0423 (9)
N(2)	0.5707 (3)	0.3997 (3)	0.3284 (1)	0.0413 (9)
H(2)	0.085 (4)	0.515 (5)	0.417 (2)	0.066 (10)
H(3)	0.053 (3)	0.283 (4)	0.505 (1)	0.049 (9)
H(4)	0.158 (3)	−0.011 (5)	0.519 (2)	0.063 (9)
H(5)	0.339 (4)	−0.129 (5)	0.447 (2)	0.073 (12)
H(7)	0.494 (3)	−0.077 (5)	0.339 (1)	0.054 (9)
H(9)	0.629 (4)	0.013 (5)	0.230 (2)	0.077 (12)
H(10)	0.670 (3)	0.237 (4)	0.143 (2)	0.067 (9)
H(11)	0.545 (3)	0.528 (5)	0.130 (2)	0.078 (11)
H(12)	0.374 (4)	0.653 (5)	0.205 (2)	0.085 (12)
H(14)	0.225 (3)	0.605 (5)	0.314 (1)	0.062 (9)
H(15)A	0.669 (3)	0.345 (4)	0.427 (1)	0.044 (8)
H(15)B	0.579 (3)	0.549 (5)	0.420 (1)	0.049 (9)

Table IV. Atomic Parameters for **6**

atom	x	y	z	U_{iso}
C(1)	0.0708 (1)	0.1007 (2)	−0.0009	0.0536 (6)
C(2)	0.1396 (1)	0.1333 (2)	−0.1067 (6)	0.0767 (9)
C(3)	0.2005 (1)	0.0603 (3)	−0.1429 (6)	0.0932 (11)
C(14)	0.0000	0.1515 (2)	−0.0449 (5)	0.0557 (9)
N	0.0784 (1)	0.0000	0.1345 (5)	0.0504 (7)
C(16)	0.0440 (2)	0.0000	0.3559 (6)	0.0566 (8)
H(2)	0.139 (1)	0.208 (2)	−0.154 (7)	0.091 (8)
H(3)	0.246 (3)	0.096 (2)	−0.186 (8)	0.135 (10)
H(14)	0.000	0.220 (2)	−0.147 (7)	0.065 (8)
H(16)	0.065 (1)	0.069 (2)	0.442 (4)	0.068 (6)

parameters simultaneously adjusted included: coordinates and anisotropic temperature coefficients for C and N atoms, coordinates and

Table V. Atomic Parameters for **7**

atom	x	y	z	U_{iso}
C(1)	0.1884 (2)	0.0015	0.6520 (2)	0.0444 (10)
C(2)	0.1187 (2)	−0.1056 (8)	0.6273 (3)	0.0641 (14)
C(3)	0.0628 (2)	−0.1327 (9)	0.7033 (4)	0.0700 (15)
C(4)	0.0692 (2)	−0.1164 (9)	0.8195 (4)	0.0757 (16)
C(5)	0.1336 (2)	−0.0704 (8)	0.8862 (3)	0.0657 (15)
C(6)	0.1995 (2)	0.0270 (7)	0.8476 (2)	0.0473 (11)
C(7)	0.2741 (2)	−0.0091 (6)	0.8938 (3)	0.0495 (12)
C(8)	0.3416 (2)	0.0251 (7)	0.8397 (2)	0.0457 (10)
C(9)	0.4123 (2)	−0.0747 (8)	0.8717 (3)	0.0631 (14)
C(10)	0.4677 (2)	−0.1220 (9)	0.7985 (4)	0.0715 (15)
C(11)	0.4604 (2)	−0.1354 (8)	0.6817 (4)	0.0705 (16)
C(12)	0.3960 (2)	−0.1067 (8)	0.6134 (3)	0.0617 (13)
C(13)	0.3295 (2)	0.0000 (7)	0.6449 (2)	0.0458 (11)
C(14)	0.2562 (2)	−0.0458 (7)	0.6005 (3)	0.0464 (11)
C(15)	0.1922 (2)	0.3650 (7)	0.7380 (3)	0.0516 (12)
C(16)	0.2676 (2)	0.4587 (8)	0.7782 (4)	0.0620 (14)
C(17)	0.3368 (2)	0.3638 (7)	0.7295 (3)	0.0538 (13)
N(1)	0.1872 (1)	0.1360 (5)	0.7453 (2)	0.0453 (9)
N(2)	0.3422 (1)	0.1345 (6)	0.7377 (2)	0.0442 (9)
H(2)	0.111 (2)	−0.182 (7)	0.557 (3)	0.084 (13)
H(3)	0.019 (2)	−0.183 (6)	0.672 (2)	0.064 (11)
H(4)	0.027 (2)	−0.172 (8)	0.859 (3)	0.096 (13)
H(5)	0.134 (2)	−0.118 (7)	0.959 (2)	0.070 (11)
H(7)	0.276 (1)	−0.080 (5)	0.964 (2)	0.044 (8)
H(9)	0.417 (2)	−0.136 (8)	0.947 (3)	0.080 (11)
H(10)	0.516 (2)	−0.162 (8)	0.831 (3)	0.102 (14)
H(11)	0.506 (2)	−0.197 (7)	0.646 (3)	0.091 (13)
H(12)	0.391 (2)	−0.163 (7)	0.540 (3)	0.079 (12)
H(14)	0.250 (2)	−0.131 (6)	0.533 (2)	0.059 (9)
H(15)A	0.148 (2)	0.421 (5)	0.774 (2)	0.059 (10)
H(15)B	0.186 (2)	0.400 (7)	0.649 (3)	0.085 (12)
H(16)A	0.275 (2)	0.445 (8)	0.869 (4)	0.128 (18)
H(16)B	0.266 (2)	0.616 (8)	0.761 (2)	0.071 (10)
H(17)A	0.384 (2)	0.428 (6)	0.764 (3)	0.078 (11)
H(17)B	0.331 (2)	0.397 (8)	0.639 (3)	0.101 (13)

isotropic B's for H atoms, a scale factor, and a secondary extinction parameter.[10] Final atomic parameters are given in Tables III–V, where the equivalent isotropic thermal parameters, for the atoms that were refined anisotropically, are in the form $U_{iso} = (\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j)/6\pi^2$. Anisotropic thermal parameters and lists of structure factors have been deposited as supplementary material.[11] Molecular dimensions are given

(10) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664–665 (eq 3).
(11) See paragraph at the end of the paper regarding supplementary material.

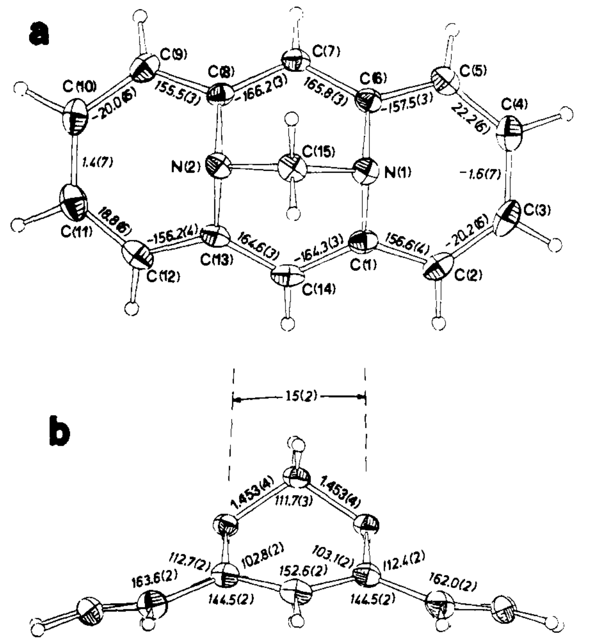


Figure 1. Molecule **5** viewed along two principal axes of inertia. (a) Numbering scheme and torsion angles along the annulene perimeter. (b) Bond distances and angle involving the carbon atom of the bridge and dihedral angles between least-squares planes. The N···N separation, 2.405 (3) Å, is shorter than both distances C(1)···C(13), 2.427 (4) Å, and C(6)···C(8), 2.426 (4) Å. Therefore, the bridge planes converge on the side of the ring plane where the methylene group is located.

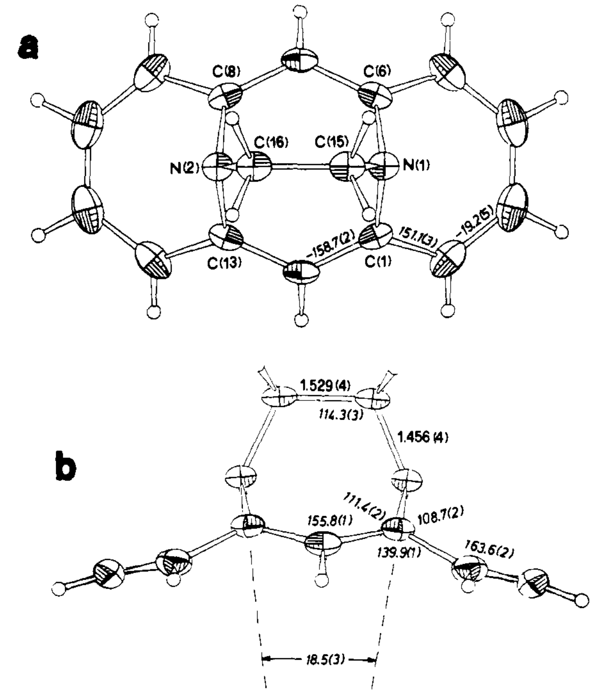


Figure 2. As in Figure 1 for compound **6**. Nonlabeled carbon atoms in (a) are numbered according to the scheme reported in Figure 1.

in Tables VI and VII and in Figures 1–3.

Correction for Thermal Libration. Molecules such as these syn-bridged annulenes were expected to behave, to a fairly good approximation, as rigid bodies in undergoing thermal libration. Consequently, the tensors **T**, **L**, and **S** were derived from the least-squares procedure proposed by Schomaker and Trueblood.[12] In these calculations, where all non-hydrogen atoms were included, equal weights were assigned to all thermal factors; the results are shown in Table VIII. In the case of **6**, owing to the *mm* crystallographic symmetry of the molecule, the off-diagonal components of **T** and **L**, and all components of **S**, except S_{12} and S_{21}, were bound to be zero. In all three molecules the agreement between observed and calculated B_{ij}'s was good, the differences rarely

(12) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sec. B* **1968**, *B24*, 63–76.

Table VI. Bond Lengths (Å), with Estimated Standard Deviations in Parentheses[a]

	compound					
	5		**6**[b]		**7**	
	uncorr	corr[c]	uncorr	corr[c]	uncorr	corr[c]
C(1)–C(2)	1.395 (5)	1.399	1.405 (3)	1.413	1.407 (5)	1.413
C(5)–C(6)	1.392 (5)	1.396			1.402 (5)	1.408
C(8)–C(9)	1.397 (4)	1.402			1.416 (5)	1.422
C(12)–C(13)	1.404 (5)	1.408			1.408 (5)	1.413
C(2)–C(3)	1.379 (5)	1.384	1.372 (4)	1.380	1.378 (6)	1.385
C(4)–C(5)	1.372 (5)	1.377			1.372 (6)	1.378
C(9)–C(10)	1.382 (5)	1.387			1.372 (6)	1.378
C(11)–C(12)	1.367 (6)	1.372			1.364 (5)	1.370
C(3)–C(4)	1.395 (6)	1.402	1.394 (4)	1.404	1.393 (7)	1.402
C(10)–C(11)	1.401 (6)	1.408			1.399 (6)	1.408
C(1)–C(14)	1.397 (4)	1.401	1.390 (2)	1.398	1.394 (5)	1.400
C(6)–C(7)	1.391 (4)	1.395			1.403 (5)	1.408
C(7)–C(8)	1.389 (4)	1.394			1.390 (5)	1.396
C(13)–C(14)	1.382 (5)	1.387			1.385 (5)	1.391
C(1)–N(1)	1.442 (4)	1.448	1.425 (2)	1.433	1.404 (4)	1.412
C(6)–N(1)	1.444 (4)	1.450			1.411 (4)	1.419
C(8)–N(2)	1.443 (4)	1.449			1.403 (4)	1.411
C(13)–N(2)	1.436 (4)	1.442			1.407 (4)	1.415
$\langle C–H \rangle_{ring}$	0.97 (4)		0.95 (5)		0.95 (3)	

[a] Bond distances involving the carbon atoms of the bridges are reported in Figures 1b, 2b, and 3b. [b] Compound **6** has crystallographic *mm* symmetry. [c] After rigid-body correction.

Table VII. Bond Angles (deg), with Estimated Standard Deviations in Parentheses[a]

	compound		
	5	**6**[b]	**7**
C(1)–C(2)–C(3)	124.9 (3)	124.3 (2)	123.5 (4)
C(4)–C(5)–C(6)	124.5 (3)		123.9 (4)
C(8)–C(9)–C(10)	124.7 (3)		123.7 (4)
C(11)–C(12)–C(13)	125.2 (3)		124.3 (4)
C(2)–C(3)–C(4)	127.1 (3)	128.0 (2)	129.1 (4)
C(3)–C(4)–C(5)	127.4 (4)		128.0 (4)
C(9)–C(10)–C(11)	126.7 (3)		128.5 (4)
C(10)–C(11)–C(12)	127.9 (4)		128.2 (4)
C(6)–C(7)–C(8)	121.6 (3)	124.8 (1)	125.4 (3)
C(13)–C(14)–C(1)	121.7 (3)		124.8 (3)
C(2)–C(1)–C(14)	126.6 (3)	123.7 (1)	123.1 (2)
C(5)–C(6)–C(7)	125.8 (3)		123.8 (3)
C(7)–C(8)–C(9)	125.8 (3)		123.3 (3)
C(12)–C(13)–C(14)	126.0 (3)		123.5 (3)
C(14)–C(1)–N(1)	118.0 (3)	122.4 (1)	122.1 (2)
C(7)–C(6)–N(1)	118.4 (3)		121.0 (3)
C(7)–C(8)–N(2)	118.2 (2)		121.9 (3)
C(14)–C(13)–N(2)	118.3 (3)		122.1 (3)
C(2)–C(1)–N(1)	115.4 (3)	113.4 (1)	114.0 (2)
C(5)–C(6)–N(1)	115.7 (3)		114.3 (3)
C(9)–C(8)–N(2)	116.0 (3)		114.0 (3)
C(12)–C(13)–N(2)	115.7 (3)		113.8 (3)
C(1)–N(1)–C(15)	109.9 (2)	118.8 (1)	123.4 (2)
C(6)–N(1)–C(15)	109.5 (2)		122.0 (3)
C(8)–N(2)–C(15)	109.7 (2)		
C(13)–N(2)–C(15)	110.2 (2)		
C(8)–N(2)–C(16)		118.8 (1)	
C(8)–N(2)–C(17)			123.0 (3)
C(13)–N(2)–C(17)			122.7 (3)

[a] Other bond angles involving the carbon atoms of the bridges, not included in this Table, are given in Figures 1b, 2b, and 3b. [b] Compound **6** has crystallographic *mm* symmetry.

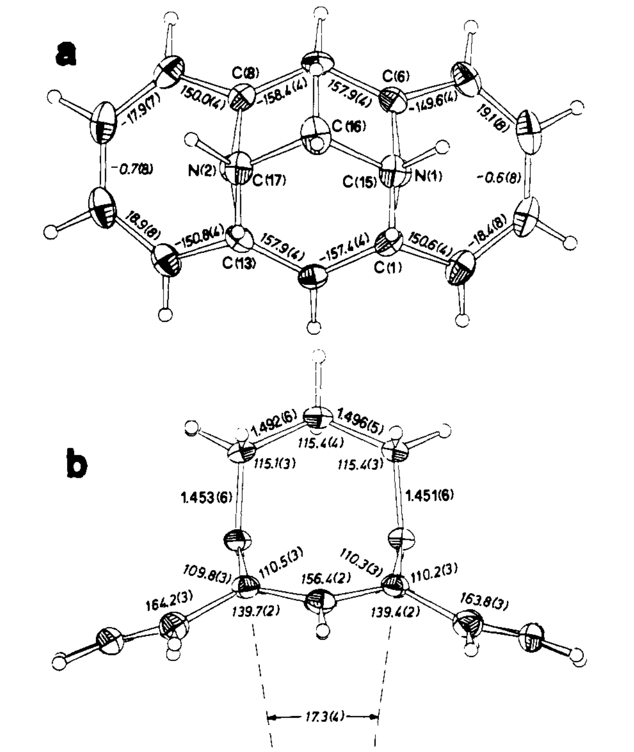


Figure 3. Views of 7 along two principal axes of inertia of the annulene nucleus.

Table VIII. Results of the Thermal-Motion Analysis[a]

	compound		
	5	6	7
ΔU_{rms},[b] $Å^2 \times 10^{-4}$	21	17	32
$\sigma_{rms}(U_{obsd})$,[c] $Å^2 \times 10^{-4}$	19	13	20
eigenvalues			
	481 (7)	642 (4)	445 (9)
T, $Å^2 \times 10^{-4}$	323 (11)	338 (6)	388 (12)
	270 (10)	257 (6)	262 (12)
	18.4 (1.6)	31.4 (0.3)	21.6 (1.2)
L, $(deg)^2$	14.7 (0.5)	15.2 (0.8)	19.3 (0.8)
	4.6 (0.5)	8.0 (0.3)	6.1 (0.5)

[a] Tensors **T**, **L**, and **S** were referred to a Cartesian coordinate system defined by unit vectors **a**, **b**, **a** × **b**. For each compound, all non-hydrogen atoms were included in the calculations. [b] $\Delta U_{rms} = \langle (U^{ij}_{obsd} - U^{ij}_{calcd})^2 \rangle^{1/2}$. [c] $\sigma_{rms}(U_{obsd}) = \langle \sigma^2(U^{ij}_{obsd}) \rangle^{1/2}$.

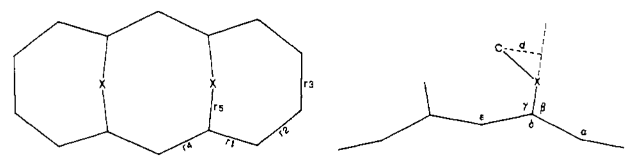
exceeding 3σ, and then only slightly.[13] Bond distances corrected for thermal motion are reported in Table VI.

Results and Discussion

The observed molecular geometry of **5** fits as a whole the *mm* symmetry; the highest differences between symmetry-related bond distances, bond angles, and absolute values of torsion angles are 0.015 Å, 1.2°, and 3.4°, respectively. The same symmetry is shown by the annulene nucleus (14 carbon atoms of the ring and 2 nitrogen atoms of the bridges) of **7**, where the overall symmetry of the molecule is very close to *m*, all differences between *m*-symmetry-related values of the molecular dimensions being less than twice their estimated standard deviation. Molecules of compound **6** have *mm* crystallographic symmetry.

No intermolecular distances less than the sum of van der Waals radii (r_C 1.7, r_N 1.5, r_H 1.2 Å) are present in the crystal structure of **5**, while that of **6** shows a single C···H contact slightly shorter than 2.9 Å, C(14)···H(14) (at x, $^1/_2 - y$, $^1/_2 + z$), 2.81 (4) Å. Two contacts of the same type are found in the molecular packing of **7**, both involving the same hydrogen atom of the bridge, H(16)B at x, $y - 1$, z, C(7)···H(16)B, 2.85 (4) Å, and C(14)···H(16)B, 2.87 (4) Å. From these findings it may be concluded that the geometry shown by the molecules of **5**, **6**, and **7** in the crystal state

Table IX. Average Geometry of the Annulene Nucleus[a]



X = N or CH

	compound		
	5	6	7
	Bond Lengths,[b] Å		
r1	1.401	1.413	1.414
	1.413	1.428	1.430
r2	1.380	1.380	1.378
	1.387	1.368	1.376
r3	1.405	1.404	1.405
	1.414	1.424	1.420
r4	1.394	1.398	1.399
	1.395	1.402	1.398
r5	1.447	1.433	1.414
	1.517	1.511	1.516
	Bond Angles, deg		
$\overline{r1r2}$	124.8	124.3	123.9
	124.7	124.7	125.0
$\overline{r2r3}$	127.3	128.0	128.5
	127.9	128.1	128.0
$\overline{r1r4}$	126.0	123.7	123.4
	124.0	120.2	118.6
$\overline{r1r5}$	115.7	113.4	114.0
	116.6	114.4	112.8
$\overline{r4r5}$	118.2	122.4	121.8
	119.2	124.5	127.3
$\overline{r4r4}$	121.6	124.8	125.1
	121.5	126.2	129.9
$\overline{r5r5}$	107.1	109.5	112.7
	104.3	102.9	102.4
	Torsion Angles,[c] deg		
Φ_1	156.5	151.1	150.3
	151.8	144.7	141.7
Φ_2	20.3	19.2	18.6
	20.8	18.6	17.6
Φ_4	165.2	158.7	157.9
	164.6	156.4	149.1
	Dihedral Angles, deg		
α	162.8	163.6	164.0
	162.4	164.2	165.1
β	112.6	108.7	110.0
	114.4	110.3	107.6
γ	102.9	111.3	110.4
	106.0	116.3	121.8
δ	144.5	139.9	139.6
	139.6	133.4	130.8
ϵ	152.7	155.8	156.5
	148.6	153.4	159.0
	Out-of-Plane Distance,[d] Å		
d	1.192	0.804	0.306
	1.222	0.984	0.875

[a] Mean of *mm*-related values. For each quantity, values in the first row refer to the *syn*-diimino derivatives (X = N), those in the second row to the corresponding hydrocarbon (X = CH). [b] After rigid-body correction. [c] Mean of absolute values of torsion angles along the annulene parameter. Φ_i is the torsion angle across the r_i bond. [d] Average value of the distance of the first carbon atom of the bridge (i.e., bonded to X) from the planes C(1)–X–C(6) and C(8)–X–C(13).

(13) Since the rigid-body interpretation of thermal parameters of the hydrocarbons **5a**, **6a**, and **7a** had been performed with the inclusion of all non-hydrogen atoms in the calculations (see ref 3b, 4b, and 5, respectively), for a correct comparison of the results here too, the carbon atoms of the bridges were included in the treatment. Deletion of the methylene carbon atoms led to virtually the same results for **5** and **6**, while for **7** a slightly improved fit was obtained, none of the differences between observed and calculated B_{ij} values now exceeding 3σ.

Table X. Geometrical Parameters Related to the Aromaticity of the Annulene System[a]

	compound		
	5	**6**	**7**
$\bar{r}$,[b] Å	1.394	1.398	1.398
	1.401	1.403	1.404
ρ,[c] Å	0.011	0.013	0.015
	0.013	0.024	0.023
τ_{rms},[d] deg	18.4	21.8	22.2
	20.5	24.8	28.0
τ_{max}, deg	24.5 (3)	28.9 (3)	30.4 (4)
	29.5 (7)	35.4 (4)	39.4 (7)
D,[e] Å	0.24	0.34	0.36
	0.28	0.43	0.53
C(1)···C(6), Å	2.321 (4)	2.328 (2)	2.345 (4)
	2.385 (6)	2.355 (3)	2.349 (7)
C(8)···C(13), Å	2.317 (4)	2.328 (2)	2.336 (4)
	2.379 (6)	2.355 (3)	2.355 (7)

[a] For each quantity, values in the second row refer to the hydrocarbon (see note a of Table IX). [b] $\bar{r} = \langle r_i \rangle$ for the 14 bond distances along the annulene perimeter, after correction for molecular libration. [c] $\rho = \langle (r_i - \bar{r})^2 \rangle^{1/2}$. [d] $\tau_{rms} = \langle \tau_i^2 \rangle^{1/2}$, where the values of the misalignment angles (τ_i) between adjacent $2p_z$ orbitals along the ring are represented by the torsion angles ϕ_i's for $|\phi_i| < 90°$ and by the quantity $(180 - |\phi_i|)$ for $|\phi_i| > 90°$. [e] $D = \langle d_i^2 \rangle^{1/2}$, the d_i's being the individual distances of the 14 carbon atoms of the ring from the least-squares plane through them.

is mainly, if not totally, dictated by intramolecular energy effects.

For the annulene nuclei of the three compounds, mean values of symmetry-related bond distances and bond and torsion angles, as well as dihedral angles between relevant planes, are collected in Table IX. The corresponding values for the three hydrocarbons 1,6:8,13-propane-1,3-diylidene[14]annulene (**5a**), 1,6:8,13-butane-1,4-diylidene[14]annulene (**6a**), and 1,6:8,13-pentane-1,5-diylidene[14]annulene (**7a**) are also listed for comparison in the same table. Some geometrical quantities related to the aromatic behavior of this class of substances are presented in Table X.

Torsion angles along the annulene ring (for individual values, see Figures 1a, 2a and 3a) measure the amount of the deviation of p_z orbitals from parallelism. In all three molecules, the largest misalignment occurs for atoms C(1), C(2), and C(3) and symmetry-related p_z orbitals. This corresponds to a general trend of syn-bridged [14]annulenes to subdivide the distortion on the annulene perimeter. On going from compound **5** to **7**, a systematic but slight increase of the values of the torsion angles is observed. However, the distortion of the ring remains sufficiently low, even in **7**, to allow a degree of cyclic conjugation comparable to that of the previously described[1] *syn*-1,6:8,13-diimino[14]annulenes **1–4**. Indeed, the values of ρ (Table X), a measure of bond alternation in the anthracene skeleton, are all within the range, 0.010–0.015 Å, found in the latter compounds.

The most remarkable structural feature of the annulenes described here becomes apparent when the conformation of their rings is compared with that of the corresponding hydrocarbons **5a**, **6a**, and **7a**. From inspection of the pertinent values (Table X) of τ_{rms} and τ_{max}, i.e., the quantities describing the torsional effects on the ring, and D, a measure of the overall bending of the annulene system, it is seen that the increase of ring deformation on going from **5** to **6** is much less than that observed for the corresponding pair of molecules **5a** and **6a**. Even more striking is the close similarity of τ and D values for compounds **6** and **7**, in spite of the different number of $-CH_2-$ groups in their bridges and in marked contrast with the large difference observed for the corresponding quantities of **6a** and **7a**. As indicated by the values of the geometrical parameters reported in Table IX, the conformational features of the two series of substances (hydrocarbons vs. N-alkylated annulenes) are directly related to the electronic properties of the atoms at the terminals of the bridge chain. Indeed, while in the three hydrocarbons, only modest angular variations, and close similarity of bond lengths, are observed at the methine site, a systematic and large change of bond distances and angles involving the nitrogen atoms is exhibited by the N-alkylated compounds. In other words, in the hydrocarbons, the increased strain resulting from the insertion of further carbon atoms in the bridging group greatly affects the conformation of the annulene ring, while in *syn*-diimino derivatives, relief from steric compression is achieved mainly by a substantial flattening at the nitrogen atoms, as documented by (i) the marked enlargement of the C_{ring}–N–C_{bridge} bond angles (Table VII), from 109.8° in **5** to 118.8° in **6** and 122.8° in **7** (mean values for **5** and **7**), (ii) the concomitant, although smaller, enlargement of the C_{ring}–N–C_{ring} bond angles ($\overline{r5r5}$ in Table IX), from 107.1° in **5** to 112.7° in **7**, and (iii) the increase of double bond character for the N–C_{ring} bond distances $r5$, with a shortening of 0.033 Å on going from **5** to **7**. As a consequence of this flattening, in molecule **7**, the carbon atoms C(15) and C(17) lie only ~0.3 Å from the C_{ring}–N–C_{ring} planes, while in **7a** the corresponding distance (d in Table IX) is about 0.9 Å.

A geometrical quantity that in all syn-bridged annulenes visualizes the main conformational features of the ring is the dihedral angle between the bridges, that is, in the present case, the angle between the plane defined by atoms C(1), N(1), and C(6) and that defined by atoms C(8), N(2), and C(13). As expected in light of the comments reported above, the dihedral angle between the bridge planes is greatly increased on going from **5a** to **6a**, where its value amounts to 0.8 (5)° and 26.0 (3)°, respectively, and becomes as large as 42.5 (5)° in **7a**. By marked contrast, and rather surprisingly, the value of this parameter is smaller in **7** than in **6**, 17.3 (4)° vs. 18.5 (3)°, respectively, with a corresponding N···N separation of 2.706 (4) Å in the former molecule and 2.727 (2) Å in the latter.

Briefly considering the geometry of the chain connecting the bridges, we notice that the N–C_{bridge} bond distance has the same value, within experimental uncertainty, in all three compounds, in contrast with the already mentioned variation of the N–C_{ring} bond length. As found in the corresponding hydrocarbons, the C(15)–C(16) bond distance of **6**, 1.529 (4) Å, is significantly longer than the two C–C bond distances in the bridge of **7** [mean value 1.494 (5) Å]. The synclinal (gauche) conformation of the five-membered chain of the latter compound is virtually identical with that found in **7a**.

Registry No. 5, 95935-55-0; **6**, 95935-56-1; **7**, 95935-57-2.

Supplementary Material Available: Lists of thermal parameters and structure factors for the three compounds described in this work (22 pages). Ordering information is given on any current masthead page.