

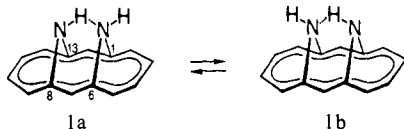
Structural Studies of *syn*-1,6:8,13-Diimino[14]annulenes. 1. Molecules without Bridge Connection

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 20133, Italy, and the Institut für Organische Chemie der Universität, Greinstrasse 4, D-5000 Köln 41, West Germany. Received August 2, 1984

Abstract: The crystal and molecular structures of *syn*-1,6:8,13-diimino[14]annulene (1), *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) have been determined by X-ray diffraction at room temperature. The molecular model obtained for 1 corresponds to a superposition of two structures related by swinging of the two imino hydrogen atoms, and the crystal structure is made of parallel ribbons which are statically or dynamically disordered. In molecule 2, the two nitrogen atoms are hydrogen-bonded, with the methyl group pointing outward. In molecule 3, both *N*-methyl groups point outward as expected. Molecule 4 has three hydrogen atoms in the region of the bridges: two of them point outward, while the third one is engaged in bonding the two nitrogen atoms. The effects of the different interactions between the bridging groups on the conformation and geometry of the annulene system of this class of compounds are discussed.

Bridged annulene chemistry is a field of continuous interest, as proved by the large number of experimental investigations and theoretical studies carried out on this subject in recent years.¹ The syntheses of novel compounds, as well as the explanation of unusual spectroscopic properties, and, in general, a better understanding of the relationship between chemical behavior and structural features, the main goals that have prompted such a conspicuous amount of work. In the case of bridged [14]annulenes with an anthracene perimeter, it has been found that the ring shows aromatic or polyenic geometry—and the molecule exhibits the corresponding chemical reactivity—according to the *syn* or *anti* position of the two bridges. In *syn*-bridged compounds, a more or less severe bending of the peripheral annulene ring is observed, depending on the nature of the bridging groups, and, when these are not connected to each other by chemical bonds, the strain imposed on the annulene ring is related to the nonbonded interactions between the atoms at the bridge sites. To our knowledge, molecules of this class of substances so far studied in great structural detail all share the common feature of bearing bridging groups that display repulsive interactions only. The recent² synthesis of *syn*-1,6:8,13-diimino[14]annulene (1), a molecule with a sterically promoted hydrogen bond between the neighboring NH groups, provides the opportunity of new insights into bridging effects on the ring skeleton of these π systems. Compound 1 is also of interest in its own right, due to the peculiar features of its intramolecular hydrogen bond. Indeed, the results of the solution studies of 1 by ¹H and ¹³C NMR spectroscopy have been interpreted² in terms of the equivalent structures 1a and 1b which are in rapid equilibrium on the NMR time scale at room temperature. When the solution was cooled, a reduced spectral



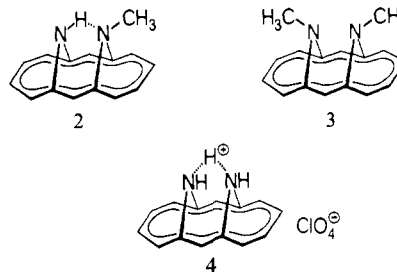
symmetry, typical of the freezing-out of the dynamic process, was observed: at 140 K, the ¹³C NMR spectrum contains seven lines instead of four found at room temperature. From line-shape analysis, values of $\Delta H^\ddagger = 26.1 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -76.5 \text{ J mol}^{-1} \text{ K}^{-1}$ were obtained for the configurational inversion of the two nitrogen atoms.

In this paper, we report a detailed X-ray structural study of 1 and 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).

Experimental Section

Crystal data for the four compounds are reported in Table I. Details of data collection and refinement are summarized in Table II. All measurements were performed at room temperature ($293 \pm 2 \text{ K}$) on an



Enraf-Nonius CAD-4 diffractometer, using graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$).

For each compound, the orientation matrix for data collection and the unit cell dimensions listed in Table I were obtained from a least-squares treatment of the automatically determined setting angles of 25 reflections with 2θ values in the range $15 < 2\theta < 32^\circ$. Reflections with net intensity $I < 0$ were classified as unobserved, except for compound 2, where a threshold limit of $I < \sigma(I)$ was assumed. Unobserved reflections were given zero weight; all other reflections were assigned variances $\sigma^2(I)$ based on counting statistics plus the additional term $(0.03S)^2$, where S is the scan count.

The intensities were measured by a variable-rate technique. The periodic monitoring of three standard reflections during the data collection showed no appreciable trend. Diffraction data were corrected for Lorentz and polarization factors but not for absorption.³

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(3) Programs used for data collection and reduction are those of the Enraf-Nonius structure determination package.

[†]Dipartimento di Chimica Fisica ed Elettrochimica, e Centro CNR, Università.

[‡]Institut für Organische Chemie der Universität.

Table I. Crystal Data

	compound			
	1	2	3	4
formula	C ₁₄ H ₁₂ N ₂	C ₁₅ H ₁₄ N ₂	C ₁₆ H ₁₆ N ₂	C ₁₄ H ₁₃ N ₂ ⁺ ·ClO ₄ ⁻
fw	208.3	222.3	236.3	308.7
crystal dimensions, mm	sphere of approxmt radius 0.14			
system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	<i>Pbcn</i> (<i>D</i> _{2h} ¹⁴ , No. 60)	<i>P</i> ₂ / <i>c</i> (<i>C</i> _{2h} ⁵ , No. 14)	<i>P</i> ₂ / <i>c</i> (<i>C</i> _{2h} ⁵ , No. 14)	<i>P</i> ₂ / <i>c</i> (<i>C</i> _{2h} ⁵ , No. 14)
<i>a</i> , Å	15.977 (2)	9.490 (2)	9.227 (1)	8.477 (2)
<i>b</i> , Å	7.329 (1)	18.777 (5)	19.463 (4)	9.735 (1)
<i>c</i> , Å	18.613 (4)	6.532 (1)	7.320 (2)	16.841 (2)
β, deg		96.89 (2)	101.03 (1)	101.61 (2)
<i>V</i> , Å ³	2179.6 (6)	1155.5 (7)	1290.3 (8)	1361.3 (5)
<i>Z</i>	8	4	4	4
ρ _{obsd} , g cm ⁻³ (flotation)	1.26	1.27	1.21	1.50
ρ _{calcd} , g cm ⁻³	1.269	1.278	1.216	1.506
<i>F</i> (000)	880	472	504	640
μ(Mo Kα), cm ⁻¹	0.71	0.71	0.68	2.94

Table II. Details of Data Collection and Refinement

	compound			
	1	2	3	4
scan type	ω	θ:2θ	ω	ω
scan rate, deg min ⁻¹	1-5	0.65-5	1.5-5	1.5-5
scan width, deg (<i>A</i> = 0.35 tan θ)	1.0 + <i>A</i>	0.8 + <i>A</i>	0.8 + <i>A</i>	1.0 + <i>A</i>
max 2θ, deg	55	55	55	55
no. of reflctns measd	2489	2634	3114	3489
no. of indep reflctns	2489	2634	2942	3104
<i>M</i> = no. of reflctns included in the refinement	1905	1589	2447	2532
<i>M</i> ₁ = no. of reflctns with <i>I</i> > 2σ(<i>I</i>)	1393	1400	1980	1940
<i>P</i> = no. of parameters refined	202	211	228	240
<i>g</i> (isotropic ext coeff) × 10 ⁶	4.7 (6)	47 (3)	10 (2)	10 (1)
<i>R</i> ^a (on <i>M</i>)	0.063	0.052	0.054	0.081
<i>R</i> (on <i>M</i> ₁)	0.038	0.043	0.040	0.059
<i>R</i> _w ^b (on <i>M</i>)	0.041	0.043	0.045	0.067
<i>S</i> ^c	1.17	1.39	1.45	1.88
convergence, largest shift	0.01σ	0.06σ	0.07σ	0.03σ
high peak in final diff map	0.16	0.24	0.16	0.44

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$. ^c $S = [\sum w(|F_o| - |F_c|)^2 / (M - P)]^{1/2}$.

All structures were solved with the program MULTAN⁴ and refined by least-squares techniques. H atom positions were found in difference maps. For 1, there were four peaks of approximately equal height (see Figure 1) near the N atoms, indicating that both imino protons are disordered, with a site occupancy of 0.5. Final refinement used this model.

In compound 4, the perchlorate anion was found to be disordered. Several different models to describe the anion in a constrained refinement⁵ were tested; in the final one, two slightly distorted tetrahedral arrangements of atoms were assumed, each with a site occupancy of 0.5. Concomitantly, the proton of the perchloric acid was represented by a two-hydrogen model.

The refinement was by minimization of the quantity $\sum w(\Delta F)^2$, with weights $w = 4F_o^2/\sigma^2(F_o^2)$ for the reflections classified as observed. In the final cycles,⁶ the sets of parameters simultaneously adjusted included coordinates and anisotropic temperature coefficients for C and N atoms, coordinates and isotropic temperature factors for H atoms, a scale factor, and a secondary extinction coefficient.⁷ For the constrained model of the anion of compound 4, 38 parameters were adjusted in the final refinement, together with those of the nonconstrained portion of the molecule. The former are the centers of mass of the two ClO₄⁻ groups, the angular displacements of the two arrangements of atoms with respect to

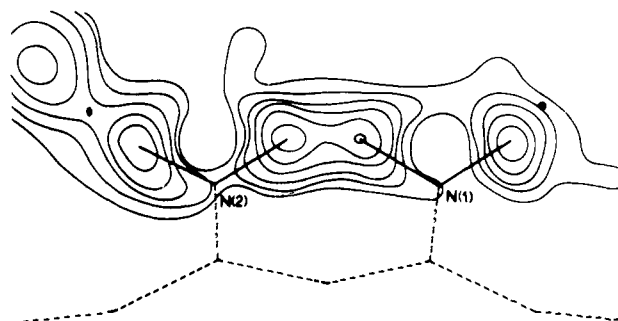


Figure 1. Difference-density synthesis in the region of the imino hydrogen atoms of compound 1, showing the distribution of each proton over two sites. The hydrogen atoms did not contribute to the calculated structure factors. Contour levels at intervals of 0.05 e Å⁻³; zero contour omitted. The map was calculated during the course of the refinement on the plane of equation 6.7724*x* - 5.6751*y* + 8.7459*z* - 0.4042 = 0, i.e., the least-squares plane through atoms N(1) and N(2), and the midpoints of the transannular distances C(1)···C(6) and C(8)···C(13). The center of symmetry ⊕ is displaced by 0.40 Å from the plane; the point of intersection of the twofold axis with the plane is denoted by ⊙.

Table III. Atomic Parameters for 1

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
C(1)	0.138 33 (9)	0.0164 (2)	0.080 62 (8)	0.0404 (5)
C(2)	0.185 58 (12)	-0.0775 (3)	0.028 50 (10)	0.0548 (6)
C(3)	0.175 41 (12)	-0.0531 (3)	-0.044 33 (10)	0.0588 (7)
C(4)	0.138 44 (12)	0.0948 (3)	-0.079 60 (9)	0.0590 (7)
C(5)	0.103 77 (11)	0.2479 (3)	-0.049 25 (9)	0.0541 (7)
C(6)	0.077 71 (9)	0.2594 (2)	0.022 95 (8)	0.0419 (5)
C(7)	0.075 04 (10)	0.4184 (3)	0.063 42 (9)	0.0455 (6)
C(8)	0.068 98 (9)	0.4258 (2)	0.138 20 (8)	0.0418 (5)
C(9)	0.087 46 (11)	0.5797 (3)	0.179 66 (10)	0.0540 (6)
C(10)	0.114 27 (12)	0.5718 (3)	0.250 33 (11)	0.0588 (7)
C(11)	0.150 69 (11)	0.4240 (3)	0.285 52 (10)	0.0572 (7)
C(12)	0.167 95 (10)	0.2541 (3)	0.257 61 (9)	0.0509 (6)
C(13)	0.129 52 (9)	0.1827 (2)	0.195 89 (8)	0.0393 (5)
C(14)	0.165 78 (10)	0.0550 (2)	0.149 91 (8)	0.0435 (5)
N(1)	0.059 57 (8)	0.0869 (2)	0.056 25 (8)	0.0403 (4)
N(2)	0.050 08 (8)	0.2637 (2)	0.178 44 (7)	0.0380 (4)
H(2)	0.229 1 (12)	-0.159 (3)	0.045 9 (10)	0.080 (6)
H(3)	0.204 4 (11)	-0.131 (3)	-0.075 1 (9)	0.063 (5)
H(4)	0.148 6 (11)	0.097 (2)	-0.133 5 (10)	0.073 (5)
H(5)	0.100 2 (11)	0.361 (3)	-0.075 7 (9)	0.060 (5)
H(7)	0.087 8 (10)	0.531 (2)	0.039 6 (8)	0.047 (5)
H(9)	0.082 9 (11)	0.698 (3)	0.156 8 (10)	0.073 (6)
H(10)	0.116 6 (11)	0.687 (3)	0.274 5 (10)	0.066 (6)
H(11)	0.175 9 (11)	0.454 (2)	0.331 7 (9)	0.064 (5)
H(12)	0.209 2 (11)	0.181 (3)	0.280 6 (9)	0.061 (5)
H(14)	0.218 1 (9)	0.006 (2)	0.164 5 (8)	0.046 (5)
H(N1)A	0.025 6 (19)	0.112 (4)	0.094 8 (18)	0.037 (8)
H(N1)B	0.037 9 (17)	0.022 (4)	0.025 3 (15)	0.029 (8)
H(N2)A	0.023 5 (17)	0.194 (4)	0.150 1 (16)	0.027 (8)
H(N2)B	0.023 0 (16)	0.293 (4)	0.218 0 (14)	0.025 (7)

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Table IV. Atomic Parameters for 2

atom	x	y	z	U_{iso}
C(1)	0.3383 (2)	0.076 42 (10)	0.0844 (3)	0.0451 (7)
C(2)	0.2490 (3)	0.083 21 (13)	-0.1038 (3)	0.0580 (9)
C(3)	0.1177 (3)	0.113 80 (13)	-0.1237 (4)	0.0624 (9)
C(4)	0.0591 (3)	0.157 25 (13)	0.0198 (4)	0.0609 (10)
C(5)	0.1215 (2)	0.178 58 (12)	0.2106 (4)	0.0551 (9)
C(6)	0.2426 (2)	0.146 46 (10)	0.3192 (3)	0.0441 (7)
C(7)	0.3423 (2)	0.182 85 (12)	0.4537 (3)	0.0492 (8)
C(8)	0.4798 (2)	0.159 20 (11)	0.5193 (3)	0.0479 (8)
C(9)	0.5887 (3)	0.204 28 (14)	0.6069 (4)	0.0615 (9)
C(10)	0.7309 (3)	0.192 37 (14)	0.5940 (4)	0.0679 (10)
C(11)	0.7894 (3)	0.150 63 (14)	0.4492 (4)	0.0670 (10)
C(12)	0.7177 (3)	0.112 01 (12)	0.2910 (4)	0.0603 (10)
C(13)	0.5757 (2)	0.090 62 (10)	0.2846 (3)	0.0483 (8)
C(14)	0.4854 (2)	0.079 31 (10)	0.1017 (4)	0.0487 (8)
C(15)	0.1563 (3)	0.022 10 (14)	0.2772 (5)	0.0617 (10)
N(1)	0.2711 (2)	0.074 00 (8)	0.2698 (2)	0.0433 (6)
N(2)	0.5241 (2)	0.087 34 (9)	0.4827 (3)	0.0507 (7)
H(2)	0.287 (2)	0.066 (1)	-0.228 (4)	0.072 (7)
H(3)	0.059 (2)	0.110 (1)	-0.256 (4)	0.069 (7)
H(4)	-0.031 (2)	0.180 (1)	-0.031 (3)	0.066 (7)
H(5)	0.084 (2)	0.220 (1)	0.271 (3)	0.062 (6)
H(7)	0.319 (2)	0.232 (1)	0.474 (3)	0.059 (6)
H(9)	0.560 (2)	0.249 (1)	0.673 (3)	0.072 (7)
H(10)	0.795 (2)	0.226 (1)	0.677 (3)	0.077 (8)
H(11)	0.892 (2)	0.156 (1)	0.442 (3)	0.068 (7)
H(12)	0.763 (2)	0.102 (1)	0.173 (4)	0.076 (8)
H(14)	0.528 (2)	0.081 (1)	-0.026 (3)	0.060 (6)
H(15)A	0.126 (2)	0.021 (1)	0.421 (4)	0.084 (8)
H(15)B	0.201 (2)	-0.025 (1)	0.257 (4)	0.084 (8)
H(15)C	0.070 (3)	0.028 (1)	0.174 (4)	0.088 (8)
H(N)	0.444 (2)	0.062 (1)	0.462 (3)	0.060 (7)

Table V. Atomic Parameters for 3

atom	x	y	z	U_{iso}
C(1)	0.0321 (2)	0.186 42 (8)	0.0814 (2)	0.0418 (5)
C(2)	-0.0830 (2)	0.233 82 (9)	0.0194 (2)	0.0513 (6)
C(3)	-0.2301 (2)	0.220 56 (9)	0.0127 (2)	0.0516 (6)
C(4)	-0.2927 (2)	0.167 00 (9)	0.1006 (2)	0.0497 (6)
C(5)	-0.2206 (2)	0.116 11 (8)	0.2120 (2)	0.0463 (5)
C(6)	-0.0691 (2)	0.099 55 (7)	0.2241 (2)	0.0364 (5)
C(7)	0.0207 (2)	0.077 49 (7)	0.3877 (2)	0.0379 (5)
C(8)	0.1750 (2)	0.078 39 (7)	0.4283 (2)	0.0378 (5)
C(9)	0.2580 (2)	0.073 88 (9)	0.6117 (2)	0.0492 (6)
C(10)	0.3929 (2)	0.105 95 (9)	0.6701 (3)	0.0546 (6)
C(11)	0.4546 (2)	0.159 06 (9)	0.5813 (3)	0.0543 (6)
C(12)	0.3936 (2)	0.191 36 (9)	0.4169 (3)	0.0528 (6)
C(13)	0.2755 (2)	0.164 91 (7)	0.2848 (2)	0.0416 (5)
C(14)	0.1717 (2)	0.206 91 (8)	0.1734 (2)	0.0446 (5)
C(15)	-0.0787 (3)	0.089 93 (13)	-0.1138 (3)	0.0678 (8)
C(16)	0.3776 (2)	0.048 33 (11)	0.2660 (3)	0.0613 (7)
N(1)	-0.0046 (1)	0.115 24 (6)	0.0674 (2)	0.0406 (4)
N(2)	0.2533 (1)	0.092 31 (6)	0.2830 (2)	0.0406 (4)
H(2)	-0.055 (2)	0.278 3 (10)	-0.015 (3)	0.066 (5)
H(3)	-0.299 (2)	0.256 8 (9)	-0.041 (2)	0.063 (5)
H(4)	-0.397 (2)	0.172 3 (8)	0.097 (2)	0.053 (5)
H(5)	-0.273 (2)	0.091 5 (8)	0.294 (2)	0.058 (5)
H(7)	-0.028 (2)	0.069 2 (7)	0.493 (2)	0.038 (4)
H(9)	0.215 (2)	0.048 3 (9)	0.704 (2)	0.059 (5)
H(10)	0.444 (2)	0.095 9 (9)	0.801 (3)	0.073 (5)
H(11)	0.544 (2)	0.180 1 (9)	0.655 (2)	0.067 (5)
H(12)	0.432 (2)	0.238 3 (10)	0.393 (2)	0.071 (5)
H(14)	0.189 (2)	0.256 3 (9)	0.183 (2)	0.057 (5)
H(15)A	-0.185 (2)	0.107 1 (9)	-0.160 (3)	0.077 (6)
H(15)B	-0.088 (2)	0.038 4 (11)	-0.107 (3)	0.078 (6)
H(15)C	-0.017 (3)	0.104 3 (11)	-0.198 (4)	0.109 (9)
H(16)A	0.469 (2)	0.053 9 (9)	0.370 (3)	0.080 (6)
H(16)B	0.345 (2)	-0.001 4 (11)	0.268 (3)	0.091 (7)
H(16)C	0.402 (2)	0.057 4 (12)	0.137 (3)	0.108 (8)

an arbitrary starting position, six internal coordinates that define the geometry of the perchlorate frame, and a unique set of T, L, and S tensors as thermal parameters of the whole anion.

Atomic scattering factors were from ref 8. Final atomic parameters are given in Tables III-VI, where the numbers in parentheses are the estimated standard deviations in the last significant digit. For the atoms

Table VI. Atomic Parameters for 4

atom	x	y	z	U_{iso}
Cl'	0.8730 (13)	0.1536 (15)	0.7003 (9)	0.0457 (5)
O(1)'	0.8250 (17)	0.2565 (16)	0.7514 (9)	0.0690 (20)
O(2)'	0.8389 (16)	0.1947 (17)	0.6194 (9)	0.1173 (40)
O(3)'	0.7901 (15)	0.0358 (17)	0.7068 (10)	0.1456 (46)
O(4)'	1.0346 (15)	0.1332 (17)	0.7227 (10)	0.1577 (42)
Cl''	0.8550 (13)	0.1390 (15)	0.7025 (9)	0.0457 (5)
O(1)''	0.8148 (17)	0.2378 (16)	0.7582 (9)	0.0669 (20)
O(2)''	0.9137 (16)	0.2032 (17)	0.6404 (9)	0.1411 (42)
O(3)''	0.7203 (15)	0.0674 (17)	0.6686 (10)	0.1269 (41)
O(4)''	0.9718 (15)	0.0540 (17)	0.7426 (10)	0.1562 (38)
N(1)	0.1597 (3)	0.1463 (3)	0.0812 (2)	0.0459 (9)
N(2)	0.3059 (3)	-0.0642 (3)	0.1333 (2)	0.0470 (10)
C(1)	0.3062 (4)	0.2257 (3)	0.1071 (2)	0.0490 (12)
C(2)	0.2999 (5)	0.3626 (4)	0.0809 (3)	0.0639 (15)
C(3)	0.1900 (5)	0.4102 (5)	0.0145 (3)	0.0725 (18)
C(4)	0.0996 (5)	0.3371 (5)	-0.0503 (3)	0.0680 (16)
C(5)	0.1027 (4)	0.1987 (5)	-0.0621 (2)	0.0582 (14)
C(6)	0.1600 (3)	0.1021 (3)	-0.0013 (2)	0.0457 (11)
C(7)	0.2258 (4)	-0.0252 (4)	-0.0113 (2)	0.0486 (12)
C(8)	0.3072 (3)	-0.1088 (3)	0.0505 (2)	0.0471 (11)
C(9)	0.4014 (5)	-0.2242 (4)	0.0460 (3)	0.0595 (15)
C(10)	0.5223 (5)	-0.2712 (5)	0.1078 (3)	0.0698 (17)
C(11)	0.6070 (5)	-0.1971 (5)	0.1735 (3)	0.0670 (16)
C(12)	0.5900 (4)	-0.0607 (5)	0.1911 (2)	0.0611 (15)
C(13)	0.4516 (4)	0.0158 (4)	0.1616 (2)	0.0485 (12)
C(14)	0.4395 (4)	0.1572 (4)	0.1505 (2)	0.0525 (12)
H(2)	0.371 (4)	0.419 (4)	0.108 (2)	0.075 (13)
H(3)	0.182 (4)	0.505 (3)	0.007 (2)	0.052 (9)
H(4)	0.054 (4)	0.394 (4)	-0.101 (2)	0.078 (11)
H(5)	0.079 (4)	0.163 (3)	-0.114 (2)	0.059 (10)
H(7)	0.222 (3)	-0.047 (3)	-0.066 (2)	0.047 (8)
H(9)	0.380 (3)	-0.263 (3)	-0.003 (2)	0.045 (9)
H(10)	0.578 (5)	-0.355 (4)	0.105 (2)	0.079 (12)
H(11)	0.702 (4)	-0.238 (3)	0.201 (2)	0.066 (11)
H(12)	0.677 (4)	-0.009 (3)	0.222 (2)	0.057 (10)
H(14)	0.533 (4)	0.207 (3)	0.167 (2)	0.069 (11)
H(N1)B	0.081 (4)	0.198 (3)	0.084 (2)	0.050 (10)
H(N1)A	0.181 (6)	0.065 (7)	0.119 (3)	0.022 (13)
H(N2)A	0.214 (6)	-0.023 (6)	0.134 (3)	0.014 (12)
H(N2)B	0.300 (3)	-0.134 (3)	0.167 (2)	0.049 (9)

Table VII. Bond Lengths (Å), with Estimated Standard Deviations in Parentheses

	compound			
	1	2	3	4
C(1)-C(2)	1.409 (2)	1.412 (3)	1.415 (2)	1.402 (5)
C(5)-C(6)	1.409 (2)	1.411 (3)	1.421 (2)	1.403 (5)
C(8)-C(9)	1.398 (3)	1.404 (3)	1.416 (2)	1.389 (5)
C(12)-C(13)	1.404 (3)	1.402 (3)	1.409 (2)	1.394 (5)
C(1)-C(14)	1.391 (2)	1.389 (3)	1.393 (2)	1.387 (5)
C(6)-C(7)	1.388 (3)	1.391 (3)	1.388 (2)	1.383 (5)
C(7)-C(8)	1.396 (2)	1.396 (3)	1.398 (2)	1.390 (4)
C(13)-C(14)	1.394 (2)	1.400 (3)	1.397 (2)	1.390 (5)
C(2)-C(3)	1.377 (3)	1.363 (4)	1.372 (2)	1.383 (6)
C(4)-C(5)	1.373 (3)	1.374 (4)	1.372 (2)	1.363 (6)
C(9)-C(10)	1.385 (3)	1.380 (4)	1.385 (2)	1.383 (6)
C(11)-C(12)	1.377 (3)	1.374 (4)	1.379 (2)	1.374 (7)
C(3)-C(4)	1.398 (3)	1.407 (4)	1.406 (3)	1.395 (6)
C(10)-C(11)	1.393 (3)	1.394 (4)	1.399 (3)	1.394 (6)
C(1)-N(1)	1.434 (2)	1.435 (3)	1.425 (2)	1.453 (4)
C(6)-N(1)	1.438 (2)	1.432 (3)	1.422 (2)	1.455 (4)
C(8)-N(2)	1.437 (2)	1.442 (3)	1.421 (2)	1.463 (4)
C(13)-N(2)	1.438 (2)	1.439 (3)	1.428 (2)	1.457 (4)
N(1)-H(N1)A	0.92 (3)			1.01 (6)
N(2)-H(N2)A	0.85 (3)	0.90 (2)		0.88 (6)
N(1)-H(N1)B	0.82 (3)			0.85 (3)
N(2)-H(N2)B	0.88 (3)			0.90 (3)
N(1)-C(15)		1.467 (3)	1.457 (2)	
N(2)-C(16)			1.456 (2)	
(C-H) _{ring}	0.96 (2)	0.97 (2)	0.98 (2)	0.93 (4)

that were refined anisotropically, the equivalent isotropic thermal parameters, in the form $U_{iso} = (\sum_i \beta_i a_i^2) / 6\pi^2$, are also given in the same tables. Anisotropic thermal parameters and lists of structure factors have been deposited as supplementary material.⁹ Individual values of the

Table VIII. Bond Angles (deg), with Esd's in Parentheses

	compound			
	1	2	3	4
C(2)-C(1)-N(1)	115.4 (2)	117.1 (2)	117.2 (1)	115.8 (3)
C(5)-C(6)-N(1)	114.7 (2)	117.2 (2)	117.4 (1)	115.6 (3)
C(9)-C(8)-N(2)	115.1 (1)	114.7 (2)	117.5 (1)	114.0 (3)
C(12)-C(13)-N(2)	114.6 (1)	114.5 (2)	117.3 (1)	115.4 (3)
C(14)-C(1)-N(1)	119.8 (1)	118.5 (2)	119.9 (1)	117.3 (3)
C(7)-C(6)-N(1)	119.9 (2)	118.5 (2)	119.3 (1)	117.3 (3)
C(7)-C(8)-N(2)	120.1 (2)	121.8 (2)	119.1 (1)	116.2 (3)
C(14)-C(13)-N(2)	120.3 (1)	121.4 (2)	119.5 (1)	116.7 (3)
C(2)-C(1)-C(14)	124.7 (2)	124.0 (2)	122.5 (1)	126.8 (3)
C(5)-C(6)-C(7)	125.2 (2)	124.0 (2)	122.8 (1)	126.9 (3)
C(7)-C(8)-C(9)	124.5 (2)	123.3 (2)	123.0 (1)	129.6 (3)
C(12)-C(13)-C(14)	124.8 (2)	123.8 (2)	122.7 (1)	127.7 (3)
C(1)-C(2)-C(3)	123.4 (2)	124.5 (2)	124.4 (2)	123.4 (4)
C(4)-C(5)-C(6)	124.1 (2)	124.6 (2)	124.1 (2)	124.7 (4)
C(8)-C(9)-C(10)	123.8 (2)	123.7 (2)	123.8 (2)	125.0 (4)
C(11)-C(12)-C(13)	123.9 (2)	124.1 (3)	124.4 (2)	123.8 (4)
C(2)-C(3)-C(4)	127.8 (2)	127.6 (2)	127.8 (2)	129.5 (4)
C(3)-C(4)-C(5)	127.7 (2)	127.7 (2)	127.8 (2)	126.5 (4)
C(9)-C(10)-C(11)	127.5 (2)	127.2 (3)	127.7 (2)	127.7 (4)
C(10)-C(11)-C(12)	127.5 (2)	127.3 (3)	127.4 (2)	127.8 (4)
C(6)-C(7)-C(8)	125.2 (2)	125.3 (2)	126.6 (1)	125.9 (3)
C(13)-C(14)-C(1)	125.1 (2)	125.6 (2)	125.6 (1)	125.3 (3)
C(1)-N(1)-C(6)	106.0 (1)	106.0 (2)	106.3 (1)	106.2 (3)
C(8)-N(2)-C(13)	105.9 (1)	104.3 (2)	105.9 (1)	107.5 (3)
C(1)-N(1)-C(15)		117.1 (2)	117.2 (1)	
C(6)-N(1)-C(15)		117.5 (2)	117.8 (1)	
C(8)-N(2)-C(16)			118.3 (1)	
C(13)-N(2)-C(16)			118.0 (1)	
<C-N-H>	109 (2)	105 (1)		110 (5)
<H-N-H>	115 (2)			109 (13)
<C-C-H>	117 (2)	117 (2)	117 (1)	117 (4)

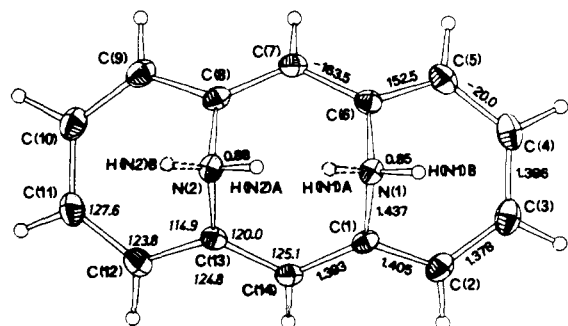


Figure 2. View of **1** along the direction corresponding to the maximum moment of inertia of the annulene nucleus. Numbering scheme, thermal ellipsoids, bond lengths, bond angles, and torsion angles along the annulene ring are reported. Thermal ellipsoids are drawn at a probability of 0.20. Hydrogen atoms, treated as isotropic, are on an arbitrary scale. The values of the molecular dimensions are averages (assuming *mm* symmetry) of the individual values listed in Tables VII-IX, where estimated standard deviations are also given. The nonlabeled hydrogen atoms were numbered according to the carbon atom to which they are bonded. The methyl carbon atom of **2** was numbered as C(15), those of **3** as C(15) and C(16).

molecular dimensions are listed in Tables VII-IX. Averaged values, assuming *mm* symmetry, are reported for compound **1** in Figure 2, which shows the atomic numbering scheme. Side views of the molecules are represented in Figure 3, where the values of some dihedral angles between planes of interest are reported, together with the value of the N...N separation, and, when appropriate, the dimensions of the intramolecular hydrogen bond.

Results and Discussion

The molecular model of **1** derived from the X-ray investigation corresponds to the superposition of the two structures **1a** and **1b**

(8) Cromer, D. T.; Waber, 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.

(9) See the paragraph at the end of the paper regarding supplementary material.

Table IX. Torsion Angles (deg) along the Annulene Perimeter, with Esd's in Parentheses

	compound			
	1	2	3	4
C(14)-C(1)-C(2)-C(3)	-152.7 (2)	-147.0 (3)	-147.0 (2)	-154.2 (4)
C(4)-C(5)-C(6)-C(7)	152.2 (2)	149.0 (3)	145.6 (2)	152.3 (4)
C(7)-C(8)-C(9)-C(10)	-152.8 (2)	-151.8 (3)	-147.4 (2)	-155.0 (4)
C(11)-C(12)-C(13)-C(14)	152.3 (2)	151.9 (3)	148.3 (2)	154.9 (4)
C(1)-C(2)-C(3)-C(4)	20.0 (3)	15.2 (4)	15.6 (3)	19.4 (8)
C(3)-C(4)-C(5)-C(6)	-19.3 (3)	-16.8 (4)	-15.1 (3)	-19.6 (7)
C(8)-C(9)-C(10)-C(11)	20.5 (3)	21.4 (5)	16.1 (3)	21.5 (7)
C(10)-C(11)-C(12)-C(13)	-20.1 (3)	-20.3 (5)	-17.3 (3)	-22.0 (7)
C(2)-C(3)-C(4)-C(5)	-0.3 (4)	0.4 (5)	-0.2 (3)	0.9 (8)
C(9)-C(10)-C(11)-C(12)	0.1 (4)	-0.9 (5)	0.6 (3)	0.6 (8)
C(13)-C(14)-C(1)-C(2)	163.8 (2)	163.1 (2)	160.2 (2)	166.3 (4)
C(5)-C(6)-C(7)-C(8)	-163.7 (2)	-161.5 (2)	-160.8 (2)	-167.9 (4)
C(6)-C(7)-C(8)-C(9)	162.9 (2)	161.9 (2)	161.5 (2)	166.9 (4)
C(12)-C(13)-C(14)-C(1)	-163.5 (2)	-162.3 (2)	-160.4 (2)	-167.1 (4)

in equal amounts. Within the limits of detection using the measured Bragg diffraction data, no splitting is observed for the positions of the non-hydrogen atoms (see below for a discussion of thermal motion). The molecule, as a whole, shows an approximate C_{2v} -*mm*2 symmetry, as indicated by the values of bond distances, bond angles, and torsion angles listed in Tables VII-IX. The apparent distance between the two endo hydrogen atoms of the imino groups is 1.19 (4) Å, while the two transannular distances C(1)...C(6) and C(8)...C(13) exhibit the same value, 2.294 (2) Å. Symmetry-averaged molecular dimensions are reported on Figure 2.

As seen in Figure 4, the crystal structure of **1** is made of parallel ribbons of molecules extending along the [001] direction. Adjacent ribbons are related by glide planes, and within each ribbon successive molecules are related to one another by centers of symmetry or twofold axes. The N(1)...N(1) contact through the inversion point is 3.103 (2) Å, whereas the N(2)...N(2) distance for two molecules related by the rotation axis amounts to 3.108 (2) Å. The corresponding distances N(1)...H(N1)B and N(2)...H(N2)B are 2.32 (2) and 2.26 (2) Å, respectively. However, between pairs of outer hydrogen atoms H(N1)B and H(N2)B, apparent contacts as short as 1.57 (4) and 1.40 (4) Å, respectively, are observed. Clearly, these two values imply that the centers of symmetry and the twofold axes refer only to an average structure but cannot be local and instantaneous symmetry operators within a given ribbon. Two interpretations of the disorder can be offered. (1) Since unacceptably short intermolecular contacts occur only between hydrogen atoms of the imino groups, it is plausible to assume as the basic frame of the crystal structure a *disorder-free* ribbon where all the imino protons of successive molecules point toward the same *z* direction, thus forming an ordered network of molecules connected by very weak hydrogen bonds. (Incidentally, we note that the resulting motif formally corresponds to an ordered alternation of molecules **1a** and **1b**). Evidently, ribbons of molecules with the imino protons pointing toward one *z* direction have the same intrinsic probability of occurrence as those with the corresponding hydrogen atoms pointing toward the opposite *z* direction. Therefore, when the electron density is averaged over the entire crystal, as happens in a diffraction experiment, an arrangement of molecules with disordered positions for the hydrogen atoms of the bridges is observed. (2) The other description of the crystal

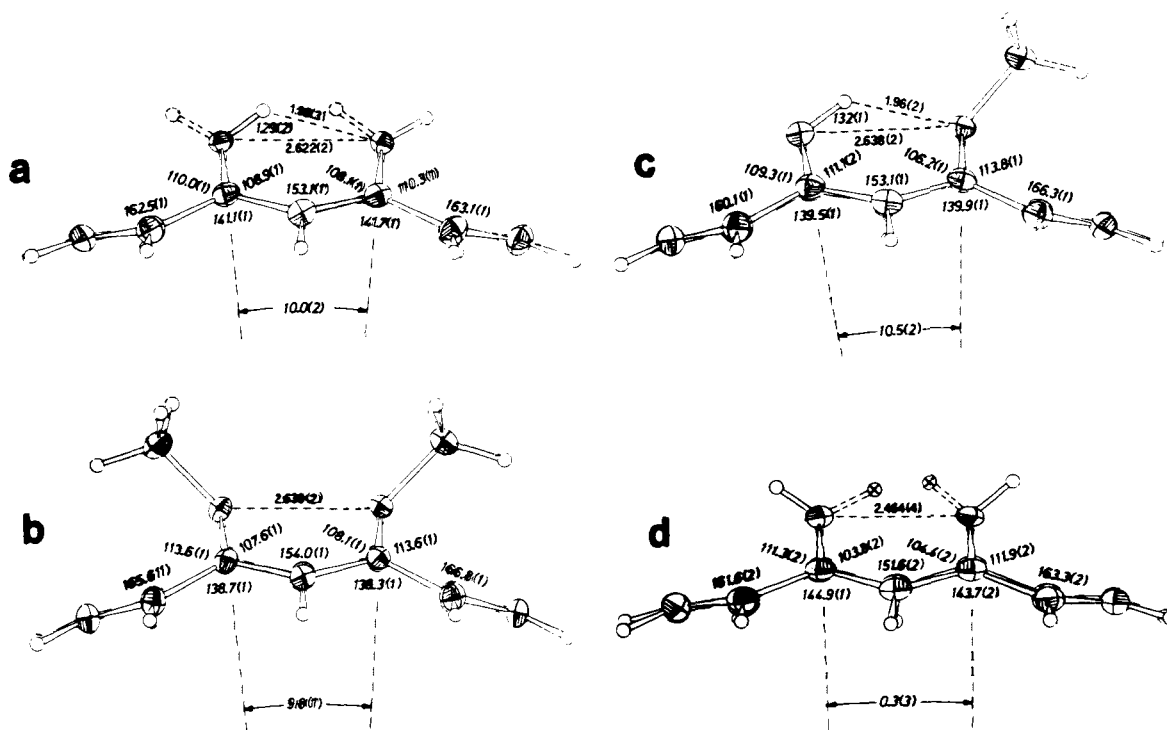


Figure 3. Side views of **1** (a), **2** (b), **3** (c), and **4** (d), with dihedral angles between least-squares planes, the N(1)...N(2) distance, and, for **1** and **2**, the parameters describing the intramolecular hydrogen bond.

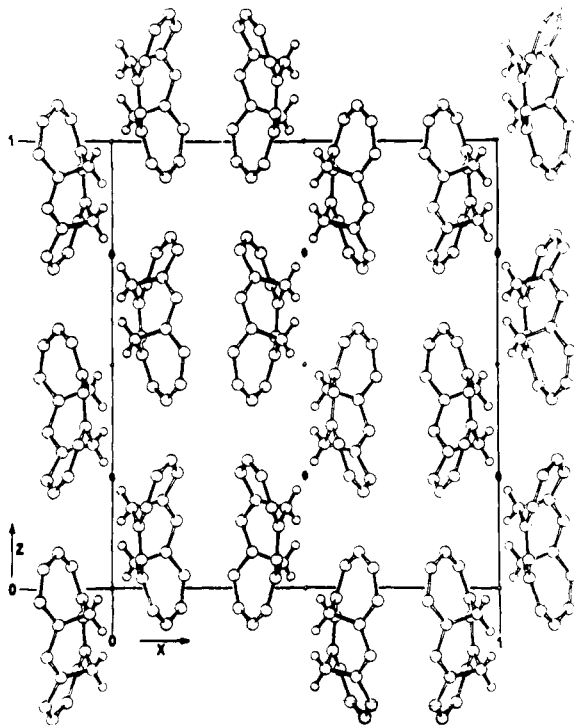


Figure 4. View of the structure of **1**, as seen down the *b* axis.

structure is obtained if, instead of the static disorder so far considered, the dynamic process $1a \rightleftharpoons 1b$ is assumed to take place in the crystal. In this instance, statistical disorder within each ribbon would be brought about by the tandem configurational inversion of the two nitrogen atoms of a given molecule and its propagation along, or simultaneous occurrence within, the chain of molecules forming the ribbon.


As usual for disordered crystals in which each molecule has two possible distinguishable orientations available to it, and the molecules are found to be distributed between the two orientations, the time scale of the observation and the potential barrier height are the key factors that determine whether the disorder qualifies

for description as static or dynamic. The peculiar feature of the present situation is that the passage from one orientation to the other simply corresponds to an intramolecular rearrangement which does not require molecular rotations nor large atomic displacements, except for the atoms of the imino groups. Therefore, while the X-ray results provide no direct information as to the kind of disorder, taken in conjunction with the NMR study,² they strongly suggest that a dynamic process may take place in the solid state. The corresponding energy barrier should be slightly higher than that in solution, owing to the presence of intermolecular very weak hydrogen bonds in the crystal structure. It is hoped that further studies, e.g., by solid-state CPMAS NMR spectroscopy, will provide additional clarification of this point.

Intramolecular Hydrogen Bond. Details of the geometry of the NH...N fragment in compounds **1** and **2** are given in Figure 3a and b, respectively. The values of the N...H contact distance and the NH...N angle reported for **1** are averages of the two distances and two angles observed in the disordered model. It can be seen that they do not differ significantly from those of **2**, where the absence of disorder allows a more accurate description of the hydrogen bond and its effects on the whole molecule. These are easily derived from a comparison of the geometry at the bridge sites of **2** and **3** (Figure 3c), the latter molecule being characterized by pure repulsive interactions between the bridging groups.¹⁰ The following features are worthy of note: (i) the formation of the intramolecular hydrogen bond affects only marginally the N...N separation; (ii) the establishment of the N(1)...H interaction modifies the N(1)-C_{ring} bond lengths, which are slightly longer in **2** than in **3**, 1.434 vs. 1.424 Å (mean values); (iii) concomitantly, the transannular distance C(1)...C(6) is larger in the former than in the latter compound [2.290 (3) vs. 2.279 (2) Å], due to the invariance of the C(1)-N(1)-C(6) bond angles; (iv) the interplay of N...N repulsion and N...H attraction in molecule **2** is reflected in significant angular deformations at the bridgehead atoms, as

(10) A close scrutiny of the intermolecular contacts in the crystal structure of **2** reveals that only two distances are less than the sum of van der Waals radii and then very slightly. They are C(4)...H(5) (at $x, 1/2 - y, -1/2 + z$), 2.84 (2) Å, and C(5)...H(11) (at $-1 + x, y, z$), 2.83 (2) Å. No short contacts are observed in **3**, with the possible exception of H(7)...H(15)C (at $x, y, 1 + z$), 2.35 (3) Å. Therefore, it is safe to assume that the molecular geometry of these two compounds in the crystalline state is mainly, if not totally, dictated by intramolecular energy effects.

Table X. Comparison of Geometrical Parameters Relative to the Annulene System in Several Bridged [14] Annulenes with an Anthracene Perimeter. Anti-Bridged Compounds are Marked with an Asterisk



	syn-bridged		anti-bridged						
	G ₂	G ₁	\bar{r} , ^a Å	ρ , ^b Å	τ_{rms} , ^c deg	τ_{max} , deg	D, ^d Å	C(1)⋯C(6), Å	C(8)⋯C(13), Å
1			1.392	0.011	20.2	27.8 (2)	0.29	2.294 (2)	2.294 (2)
2			1.393	0.014	21.2	33.0 (3)	0.33	2.290 (3)	2.274 (3)
3			1.396	0.015	22.1	34.4 (2)	0.37	2.279 (2)	2.274 (2)
4			1.388	0.010	19.0	27.7 (4)	0.23	2.325 (4)	2.356 (4)
5 ^e			1.392	0.006	17.9	25.9 (5)	0.24	2.259 (5)	2.249 (5)
6 ^f			1.396	0.013	20.7	30.1 (2)	0.31	2.470 (2)	2.472 (2)
7 ^g			1.393	0.017	23.4	34.4 (3)	0.43	2.359 (3)	2.360 (3)
8 ^h			1.385	0.020	22.5	32.6 (2)	0.35	2.340 (3)	2.326 (3)
9 ⁱ			1.397	0.018	22.0	42.1 (1)	0.34	2.278 (2)	2.341 (2)
10* ^j			1.404	0.060	34.0	75.1 (2)	0.30	2.483 (2)	2.417 (2)
11* ^k			1.408	0.058	41.0	71.4 (3)	0.29	2.502 (2)	2.440 (2)

^a Average value of the 14 bond distances, r_i , along the annulene perimeter. ^b $\rho = \langle (r_i - \bar{r})^2 \rangle^{1/2}$. ^c $\tau_{\text{rms}} = \langle \tau_i^2 \rangle^{1/2}$, 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 $|\varphi_i| < 90^\circ$, and by the quantity $(180 - |\varphi_i|)$ for $|\varphi_i| > 90^\circ$. ^d $D = \langle d_i^2 \rangle^{1/2}$, the d_i 's being the individual distances of the 14 carbon atoms of the ring from the least-squares plane through them. ^e *syn*-1,6:8,13-Diepoxy[14]annulene, ref 14. ^f *syn*-1,6:8,13-Dicarbonyl[14]annulene, ref 15. ^g *syn*-1,6:8,13-Dimethano[14]annulene, ref 16. ^h *syn*-1,6-Imino-8,13-methano[14]annulene, ref 17. ⁱ *syn*-9-Acetyl-1,6-imino-8,13-methano[14]annulene, ref 18. ^j 7-(Methoxycarbonyl)-*anti*-1,6:8,13-dimethano[14]annulene, ref 19. ^k *anti*-1,6:8,13-Bis(difluoromethano)[14]annulene at 200 K, ref 20.

shown by comparison of the two inner dihedral angles involving the bridges and the annulene frame of this molecule [111.1 (2)° and 106.2 (1)°] with those of **3** [107.6 (1)° and 108.1 (1)°, respectively].

Perchlorate Salt 4. As described in the Experimental Section, the crystal structure of this compound is affected by severe disorder of the ClO_4^- ion. The proton which interacts with the imino nitrogen atoms could not be located unambiguously, since its position apparently depends on the model adopted to interpret the disorder of the perchlorate anion. Indeed, a difference map calculated at the end of the conventional refinement (unique set of five atoms for the ClO_4^- group, which undergoes extensive and perhaps unrealistic libration) showed a single, although diffuse, peak for the hydrogen atom.¹¹ By contrast, if the anion is represented by two separate tetrahedral arrangements of atoms, two distinct positions are found for the proton,¹² suggesting a disorder caused by a sort-of intramolecular proton exchange. Some relevant features of **4**, all related to the strong interaction of the proton with the imino nitrogen atoms, can be stressed: (i) the N⋯N

intramolecular separation is reduced to the very short value of 2.464 (4) Å; (ii) the dihedral angle between the planes of the bridges, $\sim 10^\circ$ in **1**, **2**, and **3**, is here practically reduced to zero, and, consequently, a substantial flattening of the annulene ring is observed; (iii) the average N-C_{ring} bond length, 1.460 Å, is much longer than that, 1.437 Å, of the parent compound **1**; (iv) the transannular distances C(1)⋯C(6) and C(8)⋯C(13) are increased to 2.325 (4) and 2.356 (4) Å, respectively, with a possible enhancement of the aromatic character of the molecule, due to the corresponding diminished 1-6 and 8-13 overlap.

Annulene Ring. Attempts have been made¹³ to correlate some appropriate geometrical features of bridged annulenes with aromaticity. For the compounds here described, the quantities $\bar{r} = \langle r_i \rangle$, $\rho = \langle (r_i - \bar{r})^2 \rangle^{1/2}$, $\tau_{\text{rms}} = \langle \tau_i^2 \rangle^{1/2}$, and $D = \langle d_i^2 \rangle^{1/2}$, where the r_i 's are the bond distances along the annulene perimeter, τ_i 's the misalignment angles between $2p_z$ orbitals of adjacent atoms, and d_i 's the distances of each of the 14 carbon atoms of the ring from the least-squares plane through them, are reported in Table X, together with those of other syn- and anti-bridged [14]-annulenes. Collected in the table are also the largest misalignment angle, τ_{max} , and the transannular distances C(1)⋯C(6) and C(8)⋯C(13). It is seen that a discrimination between aromatic and polyenic molecules is easily made on the basis of the corresponding values of both ρ , which expresses numerically the dispersion of

(11) The centroid of this peak is not equally displaced from atoms N(1) and N(2), and the refined coordinates of the proton gave distances of 1.56 (4) and 1.16 (5) Å for N(1)⋯H and N(2)⋯H, respectively. The asymmetric position of the proton (if this model of the structure is at least a close approximation to reality) can be rationalized by the different environment of the two imino groups, particularly with respect to the anion.

(12) Preliminary investigations on **4** at ~ 170 K showed that the disorder of the perchlorate anion is maintained also at such temperature and confirmed the two-hydrogen model.

(13) (a) Bürgi, H. B.; Shefter, E.; Dunitz, J. D. *Tetrahedron* **1975**, *31*, 3089-3092. (b) Gavezzotti, A.; Simonetta, M. *Helv. Chim. Acta* **1976**, *59*, 2984-2998.

Table XI. Rigid-Body-Motion Parameters^a

	compound			
	1	2	3	4
$\Delta U_{\text{rms}},^b \text{Å}^2 \times 10^{-4}$	17	20	17	29
$\sigma_{\text{rms}}(U_{\text{obsd}}),^c \text{Å}^2 \times 10^{-4}$	9	13	8	21 ^d
eigenvalues				
T, $\text{Å}^2 \times 10^{-4}$	425 (5)	498 (6)	354 (5)	544 (8)
	306 (7)	344 (9)	322 (10)	373 (11)
	263 (11)	299 (12)	301 (8)	254 (18)
	24.2 (1.4)	22.4 (1.4)	23.2 (1.3)	18.8 (1.1)
L, (deg) ²	11.7 (0.4)	13.3 (0.7)	9.3 (0.4)	15.2 (1.9)
	5.6 (0.4)	4.8 (0.4)	5.9 (0.3)	4.7 (0.6)

^aA Cartesian coordinate system defined by the inertial axes of the annulene nucleus was used. For compounds **2** and **3**, the methyl carbon atoms were excluded from the calculations, and the values reported for **4** refer to the cation alone, with exclusion of the ClO_4^- group. ^b $\Delta U_{\text{rms}} = \langle (U_{\text{obsd}}^{ij} - U_{\text{calcd}}^{ij})^2 \rangle^{1/2}$. ^c $\sigma_{\text{rms}}(U_{\text{obsd}}) = \langle \sigma^2(U_{\text{obsd}}^{ij}) \rangle^{1/2}$. ^dThis relatively high value reflects the modest degree of precision in the atomic parameters of **4**, a direct consequence of the difficulty in interpreting the disorder of the anion (see text).

bond lengths around the mean value,²¹ and τ_{max} , perhaps more effective than τ_{rms} to gauge torsional effects. By contrast, the average deviation from planarity, as measured by the rms quantity D , can be a totally misleading feature if used to detect the presence or lack of aromaticity, as proved by the fact that the two polyenic anti compounds **10** and **11** are both more planar than most of the aromatic syn derivatives. It is true, however, that within the frame of these latter molecules, the values of D closely parallel (except for **8** and **9**)²² those of ρ and τ_{rms} , thus confirming the expected correlation between, on one side, the extent of bending of the ring (D) and its overall distortion due to torsional effects (τ_{rms}) and, on the other, the degree of bond alternation (ρ).

The ring systems of molecules **1–4** all show values of ρ , τ_{rms} , and τ_{max} which fall within the range of those of previously studied syn-bridged annulenes. This indicates that the degree of cyclic conjugation in this class of substances is only moderately affected by the nature of, and the interactions between, the bridging groups. The maximum π bond torsion is observed in compound **3**, which exhibits also the most severe bending of the ring. As seen by visual inspection (Figure 3) and by comparison of the pertinent dihedral angles, a relevant contribution to the bending is here due to nonbonded repulsive interactions between two methyl hydrogen atoms (one for each methyl group) and the outermost carbon

atoms of the ring (mean value of the four shortest C...H contacts = 2.60 Å). The reduction of this effect in molecule **2**, due to the absence of one of the CH_3 substituents, is reflected in the significant decrease of D (from 0.37 to 0.33 Å in **3** and **2**, respectively). Not surprisingly, the relevant ring distortions of **3** and **2** are accompanied by noticeable bond alternation, which is markedly reduced in **1** and **4**, the latter being the flattest of all syn-bridged annulenes so far examined.

Comparison of the transannular distances reported in Table X clearly shows that their values are mainly related to the electronic properties of the bridging groups but depend also on the aromatic or polyenic character of the ring system. Actually, in both polyenic anti compounds **10** and **11**, one of the two distances is much longer than the other, despite the identity of the two bridging groups within each molecule and in contrast with the situation observed in syn-bridged annulenes with equal transannular substituents.

Analysis of the Thermal Motion. Following the least-squares treatment proposed by Schomaker and Trueblood²³ for the anisotropic temperature factors, the tensors T, L, and S were computed for the annulene nuclei of compounds **1** to **4**. In all four cases, the 14 carbon atoms of the ring and the two nitrogen atoms of the bridges were included in the calculations, and a Cartesian coordinate system defined by the principal moments of inertia of the annulene nucleus was employed. No account was taken of the correlations between different components of the atomic vibration tensors U, and unit weight matrices were used.²⁴ The results of the treatment are given in Table XI.²⁵ Besides the expected indication of relevant anisotropy of the libration motion,²⁶ the most interesting outcome of the calculations is the substantial agreement between the mean square rotational displacements of **1** and those of molecules **2** and **3** (and, to a lesser extent, those of **4**). Also, from a close inspection of individual values of ΔU_{rms} , no anomalies could be detected in the former molecule, thus confirming that its structural disorder regards only the imino hydrogen atoms and has virtually no effect on the annulene system. While these findings are, by themselves, not sufficient to prove the occurrence of a dynamic process in the crystals of **1**, they seem, however, hardly consistent with static disorder.²⁷

Registry No. **1**, 75863-17-1; **2**, 95864-12-3; **3**, 95864-13-4; **4**, 95910-38-6.

Supplementary Material Available: Lists of thermal parameters and structure factors for all four compounds described in this work (56 pages). Ordering information is given on any current masthead page.

(14) Ganis, P.; Dunitz, J. D. *Helv. Chim. Acta* **1967**, *50*, 2369–2378.

(15) Destro, R.; Simonetta, M. *Acta Crystallogr., Sect. B* **1977**, *B33*, 3219–3221.

(16) Destro, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect. B* **1977**, *B33*, 940–942.

(17) Destro, R.; Gavezotti, A.; Simonetta, M. *Acta Crystallogr., Sect. B* **1982**, *B38*, 1352–1354.

(18) Destro, R.; Ortoleva, E.; Simonetta, M. *Acta Crystallogr., Sect. C* **1983**, *C39*, 1282–1284.

(19) Gramaccioli, C. M.; Mimun, A. S.; Mugnoli, A.; Simonetta, M. *J. Am. Chem. Soc.* **1973**, *95*, 3149–3154.

(20) Destro, R.; Simonetta, M. *Tetrahedron* **1982**, *38*, 1443–1446.

(21) For all nine syn-bridged annulenes considered in Table X, this dispersion is not random, since it is mostly due to a systematic succession of long and short bond distances in the two outer portions of the annulene perimeter, i.e., the ring fragments connecting atoms C(1) through C(6) and C(8) through C(13). The quantity ρ can therefore be assumed as a measure of bond alternation, although in a slightly different way than for polyenic anti compounds, where the alternation occurs without discontinuity in the whole ring.

(22) These two derivatives have been included in the table for the sake of completeness, but their geometrical features are to be considered with some caution. Indeed, in compound **9**, the presence of a COCH_3 substituent at atom C(9) brings about some relevant extra effects on the geometry and conformation of the ring. In fact, relief from steric hindrance between the acetyl group and the adjacent portion of the annulene system is achieved through a substantial lengthening of the C(8)–C(9) bond distance, 1.442 (2) Å, and an increase of the torsion angle C(7)–C(8)–C(9)–C(10) of about 14° with respect to the symmetrically corresponding torsion angle C(11)–C(12)–C(13)–C(14) (–137.9° and 152.1°, respectively). On the other hand, there are indications, as discussed in ref 18, that the crystal structure of the unsubstituted parent compound **8** might suffer from partial disorder, affecting particularly the geometry at the bridge sites.

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

(24) It has been pointed out (see: (a) Hirshfeld, F. L.; Shmueli, U. *Acta Crystallogr., Sect. A* **1972**, *A28*, 648–652. (b) Küppers, H.; Scheringer, C. *Ibid.* **1973**, *A29*, 306–308) that these approximations, while not strictly justifiable, do not result in serious errors when an orthogonal axial system, as in the present case, is chosen. On the other hand, the main purpose of our calculations was not an exhaustive and very accurate description of the rigid body parameters, but rather a comparison of the overall behavior of the disordered molecule **1** with that of the other three derivatives.

(25) Hirshfeld's rigid bond test (see: (a) Hirshfeld, F. L. *Acta Crystallogr., Sect. A* **1976**, *A32*, 239–244. (b) Rosenfield, R. E.; Trueblood, K. N.; Dunitz, J. D. *Ibid.* **1978**, *A34*, 828–829) indicates that these systems behave as approximately rigid bodies. The differences $\Delta_{A,B} = z_{A,B}^2 - z_{B,A}^2$, where $z_{A,B}$'s are the mean square vibrational amplitudes in the AB direction, are, on the average, slightly but systematically larger for pairs of nonbonded atoms than for connected atoms. However, it has been shown (Destro, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect. B* **1977**, *B33*, 447–456) that for systems where the quantity ΔU_{rms} is about twice as large as $\sigma_{\text{rms}}(U_{\text{obsd}})$, as in the present case (see Table XI), the rigid body model is a fairly good approximation in the analysis of the motion of molecules in crystals.

(26) Corrections to bond lengths due to thermal motion are in the range 0.004–0.008 Å for **1** and **2**, 0.003–0.007 Å for **3**, and 0.004–0.007 Å for **4**. As expected, in all four molecules, the largest increase is calculated for bond distances C(3)–C(4) and C(10)–C(11).

(27) Cases have been described where more or less extensive static disorder could be suspected or confirmed also on the basis of anomalous results of the thermal-motion analysis. See for example ref 18 and: Destro, R.; Pilati, T.; Simonetta, M. *Tetrahedron* **1980**, *36*, 3301–3304.