des fonctions amines. L'obtention de ce doublet résulte de la configuration α de la molécule (Tolman, Robins & Townsend, 1967).

L'absence de symétrie de cette structure s'observe également en solution; en effet, les protons des méthyles des cycles dioxolanes des deux ribofurannoses se présentent sous forme de quatre signaux distincts, montrant que l'anisotropie à laquelle sont soumis ces méthyles est différente pour les deux cycles ribofuranniques.

Pour l'anomère (2bβ), les protons H(C1') et H(C1") donnent un doublet à 5,76 p.p.m. avec une constante de couplage de 8 Hz identique à celle du doublet des protons aminés.

Par deutériation, ce doublet coalesce en un singulet montrant que la configuration des deux cycles ribofuranniques est β. De plus pour cet anomère, les protons des méthyles résonnent sous la forme de deux singulets à 1,33 et 1,52 p.p.m. montrant une symétrie dans la molécule.

En conclusion, l'étude par rayons-X de la quinone (2bα) a permis d'établir sans ambiguïté sa structure et de préciser la configuration et la conformation des cycles osidiques. En effet, aucune méthode spectroscopique ne pouvait permettre de localiser les substitutions sur le cycle quinonique. De plus, l'identification de cette molécule a permis de déduire la structure de son isomère (2bβ) formé au cours de la réaction.

Nous remercions la Direction de l'OCM à Abidjan qui nous a permis d'effectuer tous les calculs sur ordinateurs IBM 370-145. L'un de nous (JPD) remercie le Fonds National de la Recherche Scientifique pour le mandat de chercheur qualifié qui lui a été accordé.

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# syn-1,6-Imino-8,13-methano[14]annulene

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**Abstract.** $C_{15}H_{13}N$, monoclinic, $C2/c$, $a = 19 \cdot 125$ (4), $b = 6 \cdot 096$ (1), $c = 19 \cdot 151$ (4) Å, $\beta = 102 \cdot 98$ (1)°, $V = 2176$ (1) Å$^3$, $M_r = 207$, $Z = 8$, $D_c = 1 \cdot 26$, $D_m = 1 \cdot 23$ g cm$^{-3}$ (flotation). Computer-controlled diffractometer (Enraf–Nonius CAD-4) data, Mo $K\alpha$ radiation ($\lambda = 0 \cdot 71069$ Å), $F(000) = 880$, $\mu$(Mo $K\alpha$) = $0 \cdot 80$ cm$^{-1}$. The structure was solved by direct methods and refined to $R = 0 \cdot 065$, $R_w = 0 \cdot 051$ for 1352 reflections with $I > 0$. The molecular structure is discussed in terms of strain imposed by *syn* bridging groups and aromaticity of the annulene ring, in comparison with analogous compounds.

**Introduction.** The number of bridged [14]annulenes whose crystal structures have been determined in our laboratory is now large; these substances offer a good opportunity to gauge electronic and steric effects of substituents on molecular conformation (Destro, Pilati & Simonetta, 1980, and references therein). The title compound has been synthesized by Vogel, Brocker & Junglas (1980), and its crystal structure is presented here.

A preliminary crystallographic study was done by photographic methods and on a Syntex P1̄ diffractometer. Intensity data were collected on a CAD-4

diffractometer {$\theta/2\theta$ variable-range variable-scan; $2\theta_{max} = 47°$, due to the smallness of the crystal sample and to temperature effects; no noticeable decay during data collection; 1609 reflections, of which 257 with $I <$ 0 were given zero weight; variance $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (pI_{raw})^2]^{1/2}/Lp$, where $\sigma(I_{raw})$ was based on counting statistics, and $p = 0.025$; Lp correction; no absorption correction}.

The structure solution and refinement were accomplished by direct on-line processing of the diffraction data on the PDP-11 computer using the Enraf–Nonius structure determination package which incorporates *MULTAN* (Germain, Main & Woolfson, 1971). H atoms were refined isotropically, non-H atoms anisotropically; a secondary-extinction coefficient was included [final value: 0.62 (18) × 10⁻⁶], for a total of 198 variables; form factors were from Cromer & Waber (1974). The ambiguity between bridge C and N atoms was solved by separate least-squares/difference-map cycles in which (*a*) the bridge C and N atoms were treated isotropically and the H atoms of the bridging groups were excluded; this procedure yielded unambiguous positions for the three H atoms in the difference map, or (*b*) two equivalent H−*X*−H bridging groups were introduced; this led to an unrealistically

**Table 1.** *Final atomic coordinates and isotropic thermal parameters* (× 10) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

| | $x$ | $y$ | $z$ | $U_{eq}/U$ (Å²) |
|---|---|---|---|---|
| C(1) | 0.1405 (1) | 0.5777 (4) | 0.0623 (1) | 0.62 (1) |
| C(2) | 0.0827 (2) | 0.7210 (4) | 0.0639 (1) | 0.81 (2) |
| C(3) | 0.0232 (1) | 0.6683 (5) | 0.0891 (2) | 0.95 (2) |
| C(4) | 0.0147 (2) | 0.4914 (5) | 0.1346 (2) | 0.95 (2) |
| C(5) | 0.0644 (1) | 0.3373 (5) | 0.1631 (2) | 0.84 (2) |
| C(6) | 0.1261 (1) | 0.2887 (4) | 0.1383 (1) | 0.62 (1) |
| C(7) | 0.1898 (1) | 0.2197 (4) | 0.1811 (1) | 0.59 (1) |
| C(8) | 0.2561 (1) | 0.2253 (3) | 0.1649 (1) | 0.53 (1) |
| C(9) | 0.3213 (1) | 0.2227 (4) | 0.2172 (1) | 0.65 (1) |
| C(10) | 0.3838 (1) | 0.3189 (4) | 0.2105 (1) | 0.73 (2) |
| C(11) | 0.3927 (1) | 0.4866 (4) | 0.1627 (1) | 0.77 (2) |
| C(12) | 0.3396 (1) | 0.5896 (4) | 0.1141 (1) | 0.70 (2) |
| C(13) | 0.2707 (1) | 0.5078 (4) | 0.0879 (1) | 0.56 (1) |
| C(14) | 0.2103 (1) | 0.6383 (4) | 0.0689 (1) | 0.62 (2) |
| C(15) | 0.2646 (1) | 0.2645 (3) | 0.0910 (1) | 0.53 (1) |
| N | 0.1219 (1) | 0.3451 (3) | 0.0629 (1) | 0.74 (1) |
| H(2) | 0.090 (1) | 0.852 (4) | 0.047 (1) | 57 (5) |
| H(3) | −0.015 (1) | 0.762 (4) | 0.083 (1) | 78 (7) |
| H(4) | −0.033 (1) | 0.501 (4) | 0.152 (1) | 83 (7) |
| H(5) | 0.057 (1) | 0.255 (5) | 0.210 (2) | 100 (8) |
| H(7) | 0.187 (1) | 0.195 (4) | 0.232 (1) | 60 (5) |
| H(9) | 0.316 (1) | 0.157 (4) | 0.261 (1) | 63 (6) |
| H(10) | 0.433 (1) | 0.284 (4) | 0.246 (1) | 77 (7) |
| H(11) | 0.447 (1) | 0.559 (4) | 0.171 (1) | 74 (6) |
| H(12) | 0.350 (1) | 0.735 (4) | 0.099 (1) | 76 (6) |
| H(14) | 0.221 (1) | 0.784 (4) | 0.070 (1) | 67 (6) |
| H(151) | 0.217 (1) | 0.216 (4) | 0.056 (1) | 74 (6) |
| H(152) | 0.309 (1) | 0.203 (3) | 0.086 (1) | 37 (4) |
| H(N) | 0.063 (1) | 0.331 (4) | 0.039 (1) | 75 (6) |

**Table 2.** *Bond lengths* (Å)

| | | | |
|---|---|---|---|
| C(1)−C(2) | 1.414 (3) | C(9)−C(10) | 1.362 (3) |
| C(2)−C(3) | 1.372 (4) | C(10)−C(11) | 1.408 (3) |
| C(3)−C(4) | 1.418 (4) | C(11)−C(12) | 1.367 (3) |
| C(4)−C(5) | 1.361 (4) | C(12)−C(13) | 1.392 (3) |
| C(5)−C(6) | 1.397 (3) | C(13)−C(14) | 1.383 (3) |
| C(6)−C(7) | 1.374 (3) | C(14)−C(1) | 1.363 (3) |
| C(7)−C(8) | 1.371 (3) | | |
| C(8)−C(9) | 1.413 (3) | ⟨C−H⟩$_{ring}$ | 0.990 (23) |
| C(1)−N | 1.463 (2) | C(13)−C(15) | 1.491 (2) |
| C(6)−N | 1.469 (2) | C(15)−H(151) | 1.048 (21) |
| N−H(N) | 1.114 (22) | C(15)−H(152) | 0.953 (16) |
| C(8)−C(15) | 1.480 (2) | | |

**Table 3.** *Bond angles* (°)

| | | | |
|---|---|---|---|
| C(1)−C(2)−C(3) | 125.3 (3) | C(8)−C(9)−C(10) | 125.6 (2) |
| C(2)−C(3)−C(4) | 127.8 (3) | C(9)−C(10)−C(11) | 127.6 (2) |
| C(3)−C(4)−C(5) | 127.3 (3) | C(10)−C(11)−C(12) | 126.7 (2) |
| C(4)−C(5)−C(6) | 125.2 (3) | C(11)−C(12)−C(13) | 125.4 (2) |
| C(5)−C(6)−C(7) | 124.4 (2) | C(12)−C(13)−C(14) | 123.8 (2) |
| C(6)−C(7)−C(8) | 126.8 (2) | C(13)−C(14)−C(1) | 127.7 (2) |
| C(7)−C(8)−C(9) | 123.6 (2) | C(14)−C(1)−C(2) | 125.7 (2) |
| C(2)−C(1)−N | 114.0 (2) | C(7)−C(8)−C(15) | 121.7 (2) |
| C(14)−C(1)−N | 119.8 (2) | C(9)−C(8)−C(15) | 114.2 (2) |
| C(5)−C(6)−N | 114.9 (2) | C(12)−C(13)−C(15) | 114.7 (2) |
| C(7)−C(6)−N | 120.2 (2) | C(14)−C(13)−C(15) | 121.0 (2) |
| C(1)−N−C(6) | 105.9 (1) | C(8)−C(15)−C(13) | 103.1 (1) |
| C(1)−N−H(N) | 107.2 (11) | C(8)−C(15)−H(151) | 107.4 (11) |
| C(6)−N−H(N) | 101.9 (11) | C(8)−C(15)−H(152) | 108.6 (9) |
| | | C(13)−C(15)−H(151) | 108.7 (12) |
| | | C(13)−C(15)−H(152) | 107.9 (10) |
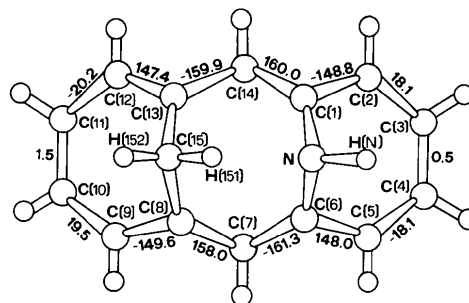


Fig. 1. Numbering scheme and torsion angles (°) for IMA (e.s.d.'s are in the range 0.2–0.4°).

high value for the thermal parameter of one H atom in the refinement. A final difference map after convergence of the full anisotropic refinement revealed no peak higher than 0.18 e Å⁻³. Tables 1–3 and Figs. 1 and 2 report the final geometric parameters of the molecular structure.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36521 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
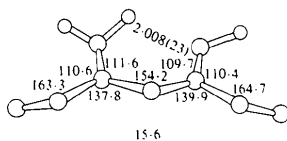
Fig. 2. Dihedral angles (°) between least-squares planes (e.s.d.'s are in the range 0·2–0·3°) and a short N···H contact (Å).

**Discussion.** The description of the molecular geometry will be given in comparison with similar compounds with different bridging groups: 'BOX' ($G_1 = G_2 = O$: Ganis & Dunitz, 1967), 'BCA' ($G_1 = G_2 = CO$: Destro & Simonetta, 1977) and 'SBM' ($G_1 = G_2 = CH_2$; Destro, Pilati & Simonetta, 1977). For the present compound (henceforth 'IMA') $G_1 = CH_2, G_2 = NH$.
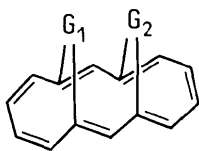


The trend of increasing $G_1 \cdots G_2$ mutual steric hindrance is BOX < BCA < IMA < SBM, as reflected by the increasing distance between bridge atoms [2·550 (4), 2·591 (2), 2·705 (3), 2·921 (3) Å, respectively] and by the dihedral angle between the two planes identified by one bridge and two bridgehead atoms (5·4, 9·9, 15·6, 26·6°, respectively). The H atom attached to the N atom in IMA points away from the methylene H atom as expected on steric grounds, and the N-atom lone-pair electrons point towards the neighbouring bridging group. The two C–N–H angles at NH are significantly different [101·9 (11) and 107·2 (11)°], while the four C–CH angles at $CH_2$ are equal within experimental error [average 108·2 (10)°]. The H–C–H angle [120·0 (15)°] is even larger than the value suggested by orthogonality of $sp^3$ hybrids [116°, given the C–C–C angle of 103·1 (1)°]. The conclusion can be drawn that the strain due to repulsion between bridging groups does not prevent the methylene group from adjusting itself to an undistorted local $C_{2v}$ symmetry, while the NH group is more perturbed. For comparison, methylene C–C–H angles in the highly strained SBM molecule varied from 115 (1) to 107 (1)°, and the two H–C–H angles were 108 (2) and 107 (1)°.

Attempts have been made to correlate some appropriate geometrical features with aromaticity (Gavezzotti & Simonetta, 1976; Bürgi, Shefter & Dunitz, 1975). The quantities $\bar{r} = \langle r_i \rangle$, $\rho = \langle (r_i - \bar{r})^2 \rangle^{1/2}$, $\tau = \langle \tau_i^2 \rangle^{1/2}$, $D = \langle d_i^2 \rangle^{1/2}$ (Destro & Simonetta, 1977), in which the $r_i$'s are the bond distances along the annulene perimeter, $\tau_i$'s the torsion angles, and $d_i$'s the distances

of the ring atoms from the least-squares plane of the ring, are for IMA 1·385 Å, 0·020 Å, 22·5°, and 0·351 Å, respectively. They are in the same range as the other three compounds, with the exception of $\bar{r}$, which is shorter for IMA (BOX, 1·392; BCA, 1·396; SBM, 1·393 Å). In fact some alternation in bond lengths does occur in IMA, with $r_i$(max.) 1·418 (4), $r_i$(min.) 1·361 (4) Å. The C(1)–N–C(6) bridge angle [105·9 (1)°] is larger than that of the bridge C(8)–C(15)–C(13) [103·1 (1)°], and the transannular C···C distances differ slightly [C(1)···C(6) 2·340 (3) Å, longer, and C(8)···C(13) 2·326 (3) Å, shorter]. These effects can probably be ascribed to the different electronic properties of the two bridging groups. On the whole, IMA can be labelled 'aromatic' on the same basis as the other three compounds.

The IMA crystal appears to be one of essentially van der Waals type. No N···N distances below 3·7 Å are present, so that the prerequisite for the formation of hydrogen bonds fails (for instance, in hydrogen-bonded methylamine the relevant N···N contacts are 3·18 and 3·27 Å; Atoji & Lipscomb, 1953). The IMA crystal is also in line with packing statistics for its class of compounds (Gavezzotti, 1981); the molecular volume $V_m$ is 202 Å$^3$, and the Kitaigorodsky packing coefficient is 0·743, denoting a close-packed crystal. The overall cell electron density $D_e$ is 0·404 e Å$^{-3}$, and the calculated sublimation energy is 96·2 kJ mol$^{-1}$; statistical values are $D_e = 0.0525\bar{Z} + 0.1983 = 0.397$ e Å$^{-3}$ (where $\bar{Z}$, the average atomic number, is $\bar{Z} = \sum Z_i/N = 3.793$ for IMA), and $E_{subl} = 0.431 \, V_m/0.8 = 108.8$ kJ mol$^{-1}$.

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