

The Crystal Structure of 8,16-Imino-*cis*[2.2]metacyclophane

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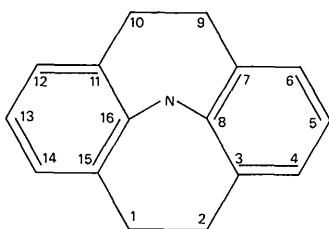
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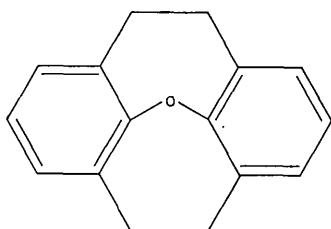
8,16-Imino-*cis*[2.2]metacyclophane, $C_{16}H_{15}N$, crystallizes in the monoclinic system with (at -160°C) space group Ia , $a=8.756$, $b=41.64$, $c=9.952$ Å, $\beta=110.6^\circ$, $Z=12$, D_m (room temperature)=1.24, $D_x=1.30$ g.cm $^{-3}$. Three-dimensional intensity data were recorded with a four-circle diffractometer and scintillation counter. The structure was determined from the Patterson synthesis and refined by block-diagonal least-squares analysis of 2975 reflexions to a final R index of 0.042. Two of the three molecules in the asymmetric unit are related by a pseudo-translation of approximately $c/2$. The C-N-C angle is 99.4° , and the dihedral angle between aromatic ring planes is 93° . Each ring is slightly distorted to a boat conformation, and the bridging bonds are stretched to a length of 1.571 Å. The molecule has no symmetry, an approximate twofold axis being necessarily violated by the pyramidal configuration of bonds to the nitrogen atom.

Introduction

8,16-Imino-*cis*[2.2]metacyclophane (I) is one of a series of derivatives of *cis*[2.2]metacyclophane prepared by Professor Boekelheide and his associates (Hess, Bailey & Boekelheide, 1967). Structure analyses have been completed for the oxido derivative (II) and for its corresponding 1,9-diene (Mathew & Hanson, 1968; Hanson & Huml, 1969). For various reasons neither of these analyses was as accurate as might be wished, and it seemed appropriate to extend the study of these compounds by the X-ray analysis of (I).



(I)



(II)

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Experimental

$C_{16}H_{15}N$, F.W. 221.3

Crystal data at room temperature: monoclinic,

$a=8.86$ (1), $b=42.20$ (4), $c=4.98$ (1) Å, $\beta=110.2$ (1) $^\circ$, $V=1747$ Å 3 , $D_m=1.24$ (2) g.cm $^{-3}$, $Z=6$, $D_x=1.26$ g.cm $^{-3}$.

Space group Cm , $C2$, or $C2/m$, from precession photographs. Consideration of the related low-temperature structure suggests that the space group is Cm . Molecular symmetry, mirror plane for one of two independent molecules.

Crystal data at -160 (10) $^\circ\text{C}$: monoclinic,

$a=8.756$ (5), $b=41.64$ (2), $c=9.952$ (5) Å, $\beta=110.6$ (1) $^\circ$, $V=3396.6$ Å 3 , $Z=12$, $D_x=1.30$ g.cm $^{-3}$, $\mu=5.9$ cm $^{-1}$.

Space group Ia (C_2^4) or $I2/a$ (C_{2h}^6) from precession photographs. Ia is confirmed by analysis. The non-standard setting is preferred because of the relationship to the symmetry of the room-temperature phase. Systematic absences, hkl for $h+k+l$ odd, $h0l$ for h or l odd.

The cell dimensions were calculated from diffractometer measurements (with narrow source and narrow slit) of the Bragg angles of selected high-angle reflexions. Cu $K\alpha$ radiation was used, with assumed wavelengths $\lambda K\alpha_1=1.54051$ Å, and $\lambda K\alpha_2=1.54433$ Å. The limits of error given above are not standard deviations, but are conservative estimates believed to allow for all possible systematic errors, including (for the low-temperature study) that caused by variation and uncertainty in the working temperature.

The material supplied consisted of colourless transparent needles (long axis, c) from which it was possible to cut approximately equi-dimensional specimens. Those used for data collection were of maximum dimension 0.4 mm. The crystal suffers a reversible phase

Table 1. *Final parameters*

(a) Final parameters of the non-hydrogen atoms

The equivalent positions are: $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + |x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, z|$.

The temperature factor is defined as

$$\exp[-2\pi^2(U_{11}a^*h^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + U_{22}b^{*2}k^2 + 2U_{23}b^*c^*kl + U_{33}c^{*2}l^2)].$$

 D_i are the r.m.s. displacements in the directions of the principal axes of the thermal-motion ellipsoids.

| Atom | x $\times 10^4$ | y $\times 10^5$ | z $\times 10^4$ | U_{11} $\text{\AA}^2 \times 10^4$ | U_{12} $\text{\AA}^2 \times 10^4$ | U_{13} $\text{\AA}^2 \times 10^4$ | U_{22} $\text{\AA}^2 \times 10^4$ | U_{23} $\text{\AA}^2 \times 10^4$ | U_{33} $\text{\AA}^2 \times 10^4$ | D_1 \AA | D_2 \AA | D_3 \AA |
|--------|--------------------|--------------------|--------------------|--|--|--|--|--|--|-----------------------|-----------------------|-----------------------|
| C1(1) | 5683(4) | 21392(7) | 2415(4) | 143(14) | -3(21) | 70(14) | 185(15) | 6(13) | 325(18) | 0.12 | 0.14 | 0.18 |
| C1(2) | 4043(4) | 23295(7) | 2105(4) | 108(14) | -4(10) | 22(13) | 138(14) | -35(13) | 309(18) | 0.10 | 0.12 | 0.19 |
| C1(3) | 2497(4) | 21324(7) | 1519(4) | 101(13) | -4(10) | 66(12) | 158(14) | -61(12) | 247(16) | 0.09 | 0.11 | 0.17 |
| C1(4) | 1328(4) | 21706(7) | 146(4) | 126(15) | 57(11) | 126(15) | 194(15) | 13(12) | 235(16) | 0.10 | 0.15 | 0.16 |
| C1(5) | 36(4) | 19577(8) | -360(4) | 127(15) | 42(12) | 22(12) | 300(17) | -7(13) | 180(16) | 0.10 | 0.12 | 0.19 |
| C1(6) | -79(4) | 16960(8) | 456(4) | 118(13) | -46(12) | 51(12) | 284(17) | -113(13) | 217(15) | 0.10 | 0.15 | 0.16 |
| C1(7) | 1087(4) | 16491(8) | 1829(4) | 184(14) | -52(11) | 113(13) | 251(16) | -78(12) | 204(16) | 0.10 | 0.12 | 0.18 |
| C1(8) | 2276(4) | 18838(7) | 2660(4) | 181(14) | 18(11) | 33(11) | 236(15) | -62(12) | 127(14) | 0.10 | 0.11 | 0.17 |
| C1(9) | 1150(5) | 13404(8) | 2660(4) | 298(18) | -128(14) | 162(15) | 274(17) | -69(14) | 250(17) | 0.12 | 0.15 | 0.24 |
| C1(10) | 2856(5) | 11792(9) | 3248(4) | 375(20) | -135(15) | 32(15) | 279(18) | 78(14) | 211(17) | 0.12 | 0.14 | 0.21 |
| C1(11) | 4281(4) | 12977(8) | 3087(4) | 262(18) | -17(12) | -46(14) | 174(15) | 54(13) | 185(16) | 0.10 | 0.13 | 0.21 |
| C1(12) | 5187(4) | 11079(7) | 2456(4) | 249(17) | 26(12) | -82(14) | 160(15) | 11(13) | 230(17) | 0.10 | 0.13 | 0.22 |
| C1(13) | 6332(4) | 12448(8) | 1963(4) | 199(16) | 79(13) | -45(14) | 247(16) | -104(14) | 230(17) | 0.11 | 0.12 | 0.23 |
| C1(14) | 6510(4) | 15771(8) | 1959(4) | 103(14) | 36(12) | -22(12) | 288(17) | -30(13) | 169(15) | 0.09 | 0.15 | 0.18 |
| C1(15) | 5633(4) | 17591(7) | 2552(3) | 109(13) | 29(10) | -16(11) | 164(14) | -12(11) | 117(13) | 0.08 | 0.12 | 0.15 |
| C1(16) | 4633(4) | 16287(7) | 3183(3) | 165(14) | -13(11) | -28(11) | 173(14) | -20(11) | 82(13) | 0.07 | 0.13 | 0.16 |
| N1 | 3622(3) | 1834(6) | 3685(3) | 208(13) | -57(10) | 84(11) | 223(13) | -41(10) | 165(13) | 0.12 | 0.13 | 0.17 |
| C2(1) | 5620(4) | 21089(8) | 7449(4) | 102(14) | -25(11) | 61(14) | 230(16) | -53(14) | 355(19) | 0.10 | 0.15 | 0.20 |
| C2(2) | 3979(4) | 22922(7) | 7217(4) | 146(15) | -4(11) | 53(14) | 188(15) | 4(13) | 312(18) | 0.12 | 0.14 | 0.18 |
| C2(3) | 2446(4) | 20916(7) | 6648(3) | 116(14) | 12(10) | 47(12) | 208(15) | -64(12) | 197(15) | 0.10 | 0.12 | 0.17 |
| C2(4) | 1246(4) | 21358(8) | 5313(4) | 167(15) | 70(12) | 23(13) | 254(17) | -15(13) | 210(16) | 0.11 | 0.14 | 0.18 |
| C2(5) | -42(4) | 19171(8) | 4827(4) | 124(15) | 38(12) | 32(13) | 284(17) | -51(13) | 236(17) | 0.11 | 0.14 | 0.19 |
| C2(6) | -67(4) | 16446(8) | 5020(4) | 117(13) | -24(11) | 87(12) | 274(17) | -127(13) | 225(15) | 0.10 | 0.12 | 0.17 |
| C2(7) | 1143(4) | 15918(7) | 6955(3) | 158(14) | -29(11) | 80(12) | 256(16) | -73(12) | 150(15) | 0.10 | 0.13 | 0.19 |
| C2(8) | 2323(4) | 18326(7) | 7488(3) | 111(14) | -2(11) | 46(12) | 257(16) | -62(12) | 147(15) | 0.10 | 0.12 | 0.17 |
| C2(9) | 1281(4) | 12797(8) | 7783(4) | 263(16) | -85(12) | 136(14) | 230(16) | -70(13) | 234(17) | 0.13 | 0.13 | 0.19 |
| C2(10) | 3006(5) | 1125(8) | 8493(4) | 319(18) | -62(14) | 37(14) | 266(18) | 54(13) | 154(15) | 0.11 | 0.15 | 0.20 |
| C2(11) | 4375(4) | 12565(7) | 8050(3) | 227(16) | 26(12) | -24(14) | 149(15) | -4(12) | 206(16) | 0.10 | 0.14 | 0.18 |
| C2(12) | 5251(4) | 10750(7) | 7405(4) | 264(17) | 54(12) | -51(14) | 149(15) | -4(12) | 206(16) | 0.10 | 0.13 | 0.22 |
| C2(13) | 6324(4) | 12242(8) | 6852(4) | 162(15) | 112(13) | -23(13) | 296(17) | -69(14) | 207(16) | 0.10 | 0.13 | 0.22 |
| C2(14) | 6471(4) | 15279(8) | 6982(4) | 118(14) | 44(12) | 25(12) | 320(18) | -48(13) | 157(15) | 0.10 | 0.13 | 0.19 |
| C2(15) | 5621(4) | 17469(7) | 7544(4) | 72(13) | 41(10) | -11(11) | 136(15) | -31(12) | 173(15) | 0.08 | 0.14 | 0.16 |
| C2(16) | 4681(4) | 15862(7) | 8214(3) | 145(14) | 21(11) | 21(2) | 213(15) | -28(11) | 138(15) | 0.10 | 0.13 | 0.16 |
| N2 | 3701(3) | 17801(6) | 8785(3) | 194(12) | -14(10) | 9(10) | 245(14) | -36(10) | 102(11) | 0.09 | 0.14 | 0.14 |
| C3(1) | 2872(4) | 2151(8) | 2082(5) | 182(16) | 5(12) | 108(16) | 210(17) | 11(15) | 508(24) | 0.13 | 0.15 | 0.23 |
| C3(2) | 3021(4) | -1577(8) | 2174(5) | 176(15) | 65(12) | 139(16) | 220(17) | 45(15) | 515(23) | 0.11 | 0.16 | 0.23 |
| C3(3) | 1469(4) | -3401(7) | 1486(4) | 236(15) | 54(11) | 122(14) | 157(15) | 79(12) | 287(17) | 0.11 | 0.14 | 0.18 |
| C3(4) | 1242(5) | -5662(8) | 378(4) | 419(19) | 70(13) | 204(18) | 150(15) | 38(13) | 291(18) | 0.11 | 0.14 | 0.21 |
| C3(5) | -265(5) | -7059(8) | -306(4) | 541(22) | 37(14) | 111(16) | 156(15) | 3(12) | 172(16) | 0.12 | 0.13 | 0.24 |
| C3(6) | -1605(5) | -6158(8) | 66(4) | 372(19) | -58(13) | 31(14) | 170(16) | 20(12) | 198(15) | 0.12 | 0.14 | 0.18 |
| C3(7) | -142(4) | -3957(7) | 1162(3) | 229(15) | 36(12) | 45(12) | 199(15) | 69(12) | 166(14) | 0.10 | 0.14 | 0.18 |
| C3(8) | 151(4) | -284(7) | 1924(3) | 214(15) | 20(11) | 39(11) | 152(14) | 18(15) | 260(17) | 0.12 | 0.16 | 0.21 |
| C3(9) | -2880(4) | -2601(9) | 1453(4) | 174(15) | -81(13) | 55(13) | 369(20) | 38(10) | 133(13) | 0.10 | 0.13 | 0.15 |
| C3(10) | -2939(4) | 1148(9) | 1666(4) | 165(15) | 20(13) | 99(14) | 354(19) | -38(14) | 321(18) | 0.12 | 0.16 | 0.20 |
| C3(11) | -1708(4) | 3155(7) | 1301(4) | 185(15) | 22(11) | 65(12) | 208(15) | -80(12) | 213(15) | 0.11 | 0.14 | 0.18 |
| C3(12) | -2104(4) | 5550(8) | 245(4) | 232(15) | 80(12) | 194(13) | 238(17) | -55(12) | 208(15) | 0.12 | 0.13 | 0.21 |
| C3(13) | -894(4) | 6989(8) | -145(4) | 324(17) | 29(12) | 7(14) | 163(15) | -16(12) | 201(15) | 0.13 | 0.13 | 0.21 |
| C3(14) | 705(4) | 5951(7) | 443(4) | 315(17) | -60(12) | 151(14) | 156(15) | -59(13) | 286(17) | 0.11 | 0.14 | 0.16 |
| C3(15) | 1165(4) | 3581(8) | 115(4) | 151(13) | -11(10) | 61(12) | 181(14) | -29(11) | 231(15) | 0.10 | 0.14 | 0.16 |
| C3(16) | -38(4) | 2384(7) | 1977(3) | 195(14) | 0(10) | 52(12) | 144(14) | -48(11) | 140(13) | 0.09 | 0.14 | 0.14 |
| N3 | 410(3) | -287(6) | 2955(3) | 200(12) | -31(10) | 60(9) | 190(13) | -51(10) | 161(11) | 0.13 | 0.14 | 0.14 |

Table 1 (cont.)

(b) Final parameters of the non-hydrogen atoms

Equivalent positions as in (a).

| Atom | x $\times 10^3$ | y $\times 10^4$ | z $\times 10^3$ | B^2 \AA^2 |
|---------|--------------------|--------------------|--------------------|-------------------------|
| H1(1A) | 599(5) | 2174(10) | 159(5) | 0.6(10.7) |
| H1(1B) | 648(5) | 2233(9) | 240(5) | -0.2(10.9) |
| H1(2A) | 391(4) | 2501(6) | 431(4) | -0.6(10.6) |
| H1(2B) | 406(5) | 2435(11) | 306(5) | 0.8(10.9) |
| H1(3) | 148(5) | 2343(9) | -47(5) | 0.1(10.7) |
| H1(5) | -85(5) | 1978(9) | -134(4) | -0.2(10.7) |
| H1(6) | -96(5) | 1531(9) | 0(4) | -0.0(10.7) |
| H1(9A) | 684(5) | 1385(9) | 364(5) | -0.2(10.7) |
| H1(9B) | 47(5) | 1185(11) | 194(5) | 0.4(10.8) |
| H1(10A) | 322(5) | 1668(10) | 949(5) | 0.4(10.7) |
| H1(10B) | 257(5) | 942(9) | 316(4) | 0.2(10.7) |
| H1(12) | 500(4) | 886(9) | 244(4) | -0.8(10.6) |
| H1(13) | 688(6) | 1107(11) | 156(6) | 1.3(10.9) |
| H1(14) | 719(5) | 1666(9) | 149(4) | -0.3(10.8) |
| H1(16) | 333(6) | 1716(11) | 431(5) | 0.9(10.9) |
| H2(1A) | 596(7) | 2159(13) | 656(6) | 2.4(11.1) |
| H2(1B) | 643(5) | 2175(9) | 898(4) | -0.2(10.6) |
| H2(2A) | 388(5) | 2482(9) | 652(4) | -0.2(10.6) |
| H2(2B) | 404(4) | 2380(8) | 409(4) | -0.7(10.5) |
| H2(4) | 124(5) | 2321(10) | 47(5) | 0.1(10.7) |
| H2(5) | -94(5) | 1940(9) | 363(4) | -0.1(10.7) |
| H2(6) | -93(5) | 1501(9) | 526(4) | -0.6(10.6) |
| H2(9A) | 81(5) | 1310(10) | 194(5) | 0.1(10.7) |
| H2(9B) | 54(6) | 1148(11) | 713(5) | 0.7(10.9) |
| H2(10A) | 332(5) | 1136(10) | 960(5) | 0.5(10.8) |
| H2(10B) | 291(5) | 894(9) | 316(4) | 0.2(10.7) |
| H2(12) | 514(5) | 861(10) | 734(5) | 0.4(10.7) |
| H2(13) | 686(6) | 1110(12) | 640(6) | 1.5(11.0) |
| H2(14) | 723(5) | 1657(10) | 60(5) | 0.5(10.7) |
| H2(16) | 353(5) | 1679(10) | 930(5) | 0.5(10.8) |
| H3(1A) | 356(9) | 315(17) | 310(8) | 3.9(11.3) |
| H3(1B) | 363(8) | 314(15) | 139(7) | 3.1(11.4) |
| H3(2A) | 355(5) | -241(10) | 316(5) | 0.3(10.4) |
| H3(2B) | 384(9) | -242(16) | 17(8) | 4.1(11.5) |
| H3(4) | 224(5) | -61(14) | 10(5) | 0.2(10.7) |
| H3(5) | -48(6) | -849(12) | -112(6) | 1.8(11.0) |
| H3(6) | -268(5) | -71(9) | -42(4) | -0.3(10.6) |
| H3(9A) | -348(6) | 309(12) | 65(5) | 0.4(10.8) |
| H3(9B) | -297(6) | -362(11) | 47(5) | 0.6(10.8) |
| H3(10A) | -396(5) | 181(10) | 115(5) | 0.3(10.8) |
| H3(10B) | -246(6) | 175(11) | 77(5) | 0.6(10.8) |
| H3(12) | -329(5) | 625(9) | -18(4) | -0.5(10.6) |
| H3(13) | -119(4) | 876(6) | -80(4) | -0.7(10.5) |
| H3(14) | 155(5) | 686(10) | 19(5) | 0.4(10.8) |
| H3(16) | -32(5) | -39(10) | 159(5) | 0.7(10.8) |

change on cooling to -160°C , accompanied by the appearance of a class of weak reflexions. The l index for these is $n + \frac{1}{2}$ with respect to the cell at room temperature, or $2n + 1$ with respect to the cell measured at -160°C . These reflexions went unnoticed at first, and by the time they were discovered the original specimen had decomposed. The intensities of the new reflexions had therefore to be measured for a new, somewhat smaller specimen.

The intensity data were measured by the θ - 2θ scan method, using a manually operated four-circle diffractometer and scintillation counter. Nickel-filtered Cu $K\alpha$ radiation was used, with pulse-height discrimination. The specimen was maintained at $-160(10)^\circ\text{C}$ by immersion in a stream of cold gaseous nitrogen which was itself surrounded by an envelope of dry nitrogen at room temperature. The working temperature was measured by substituting a copper-constantin thermocouple for the crystal, but it was not monitored during the experiment. A reasonably strong reflexion (the same for both crystals) was scanned periodically, and the counts recorded were used in subsequent scaling of the data. A reflexion was considered to be unobserved if its net count was less than ten, or less than 20% of the total count. All independent accessible reflexions, (that is, those for which $2\theta \leq 165^\circ$) were

scanned. For reflexions with l even, 1810 of a possible 1920 were observed above background, and the range of intensities was 1 to 12,000. For those with l odd,

1165 of a possible 1856 were observed, and the range of intensities was only 1 to 32. Absorption corrections were not applied.

Table 2. Observed and calculated structure amplitudes, x 10

Table with multiple columns for observed and calculated structure amplitudes, including indices like L, F, O, C and values for various reflections. Includes an asterisk for unobserved reflexions.

external bisectors of the angles C–N–C; during refinement they moved decisively to the positions reported. Physically reasonable starting positions were assumed for the remaining hydrogen atoms. The refinement proceeded smoothly to the final parameters given in Table 1. In the final cycle, no coordinate shift was greater than 0.001 Å, or 40% of the corresponding estimated standard deviation. During the refinement, the relative positions of the centroids of the molecules related by the pseudo-translation changed by about 0.17 Å from 0 0 $\frac{1}{2}$.

The agreement residual ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) is 0.042 for the 2975 observed reflexions. For reflexions with l even and l odd, the values of R are 0.034 and 0.065 respectively. In comparing these figures, it should be remembered that the reflexions with l odd are all very weak, and thus relatively inaccurate because of unfavourable counting statistics. Observed and calculated structure amplitudes are given in Table 2; the agreement is satisfactory, and there can be no doubt of the essential correctness of the proposed structure. The nominal accuracy of the coordinates is such that the e.s.d. of the distances between non-hydrogen atoms is 0.004 to 0.006 Å. It is possible to test this estimate by comparison of chemically equivalent bond lengths, as in Table 3. While the molecule deviates appreciably from $mm2$ symmetry, there seems no reason why individual bond lengths should be affected, and these have been compared as though the molecule did indeed have this symmetry. Thus for each bond type there are 6 or 12 independent measures. A study of individual

deviations from mean values indicates a standard deviation of 0.006 Å, and the greatest deviation from the appropriate mean value is 0.015 Å. This result suggests that the e.s.d.'s derived from the normal equations of the least-squares analysis are realistic.

Thermal motion

The thermal motion of individual atoms (specified in Table 1, and illustrated in Fig. 1) is sufficiently large and anisotropic that the effect on the observed bond lengths should be considered. An attempt was made to characterize the motion in terms of rigid-body modes, using the methods of Cruickshank (1956). It was assumed (without proof, but with some qualitative support from the thermal ellipsoid plots) that the centre of libration of each molecule coincided with the centroid of its equally-weighted non-hydrogen atoms. The analysis indicated that the maximum amplitude of libration of any molecule about any axis was 3.2° , a value too small to cause significant errors in bond lengths. However, the hypothesis of pure rigid-body motion was not well supported. The root mean square deviation of calculated from observed values of U_{ij} was about 0.005 Å² for each molecule, whereas the mean e.s.d. of observed values of U_{ij} is 0.0015 Å². There are moreover some rather large individual discrepancies. Study of the molecular conformation reveals that the thermal motion is likely to be non-rigid, and the analysis therefore invalid. Each molecule is somewhat twisted, as shown in Fig. 3; the

Table 3. Bond lengths (in Å) and e.s.d.'s for the molecules 1, 2 and 3

Mean values and their standard deviations are given also.

| Bond | 1 | 2 | 3 | Mean |
|-------|-----------|-----------|------------|-----------|
| 1—2 | 1.572 (5) | 1.570 (5) | 1.558 (5)* | 1.571 (2) |
| 9—10 | 1.569 (6) | 1.567 (6) | 1.579 (5) | |
| 2—3 | 1.513 (5) | 1.512 (5) | 1.513 (5) | |
| 7—9 | 1.519 (5) | 1.521 (5) | 1.515 (5) | 1.516 (1) |
| 10—11 | 1.511 (6) | 1.520 (5) | 1.510 (5) | |
| 15—1 | 1.521 (4) | 1.510 (4) | 1.521 (5) | |
| 8—N | 1.441 (4) | 1.440 (4) | 1.438 (4) | 1.439 (1) |
| 16—N | 1.438 (4) | 1.435 (4) | 1.438 (4) | |
| 3—4 | 1.399 (5) | 1.386 (5) | 1.388 (5) | |
| 6—7 | 1.403 (5) | 1.395 (5) | 1.386 (5) | 1.393 (2) |
| 11—12 | 1.391 (5) | 1.385 (5) | 1.388 (5) | |
| 14—15 | 1.393 (5) | 1.397 (5) | 1.402 (5) | |
| 4—5 | 1.387 (5) | 1.400 (5) | 1.382 (6) | |
| 5—6 | 1.383 (5) | 1.387 (5) | 1.400 (6) | 1.390 (2) |
| 12—13 | 1.385 (6) | 1.391 (5) | 1.398 (6) | |
| 13—14 | 1.393 (5) | 1.395 (5) | 1.383 (6) | |
| 3—8 | 1.387 (4) | 1.391 (5) | 1.396 (5) | |
| 7—8 | 1.389 (5) | 1.403 (5) | 1.402 (5) | 1.396 (2) |
| 11—16 | 1.404 (5) | 1.397 (4) | 1.411 (5) | |
| 15—16 | 1.391 (5) | 1.399 (5) | 1.384 (5) | |

* This value omitted from calculation of mean.

Mean C—H 0.99 Å (0.89–1.10 Å)
Mean N—H 0.89 Å (0.88–0.90 Å)

degree of twist is different for each molecule, and is presumably determined by packing forces. Resistance to twisting must therefore be rather small, and twisting modes may contribute appreciably to the thermal motion. Such twisting could cause the terminal atoms of the bridging bonds [C(1)–C(2) and C(9)–C(10)] to undergo, relative to each other, what Busing & Levy (1964) have described as ‘highly correlated anti-parallel displacements.’ Such displacements would, of course, be equal for the two atoms involved, normal to the bond, and parallel to the approximate mirror plane which bisects the phenyl rings [that is, parallel to the plane of projection of Fig. 2(a)]. The thermal motion ellipsoids of the terminal atoms of the bridging bonds are shown in Fig. 1(d), the direction of view being that of Fig. 2(a). It appears that anti-parallel displacements may be occurring for the atoms C(1) and C(2) of each molecule, but that C(9) and C(10)

are unaffected. The effect is particularly pronounced for C3(1) and C3(2), and this bridging bond is in fact observed to be somewhat shorter than the mean for the other five. The difference of 0.013 Å is significant at the 1% level. No correction has been attempted, as the degree of correlation is quite unknown; the correction could be as large as 0.04 Å! However, it seemed prudent to omit this distance from the calculation of the mean for the bond type, even though the omission has little practical effect. The most important conclusion of the study of thermal motion is negative: since the most vulnerable bond is so little affected by twisting modes, the effect on the others is likely to be completely negligible.

Discussion

The molecular geometry is summarized in Tables 3, 4 and 5, and Figs. 2 and 3. Significant tension in the

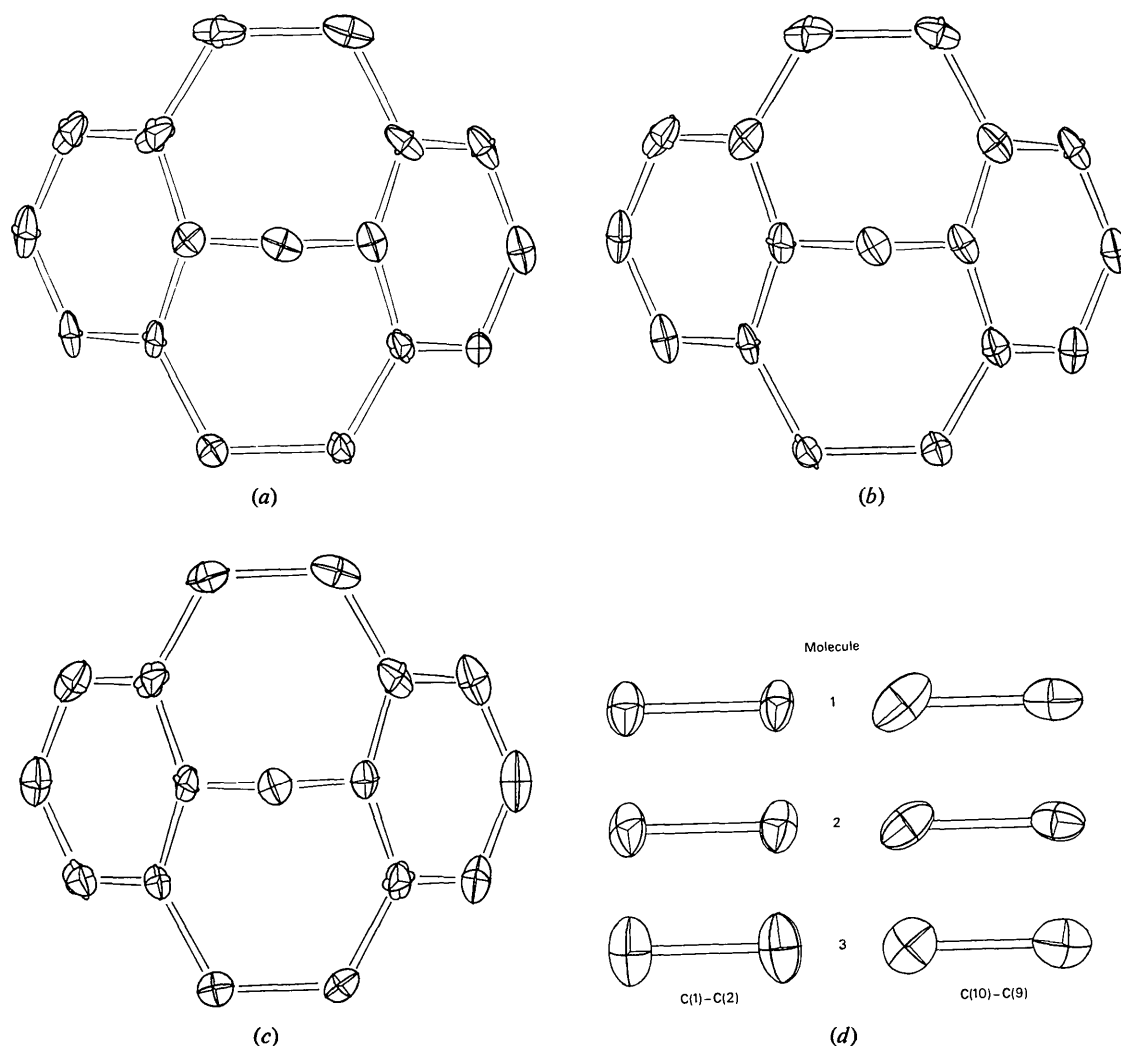


Fig. 1. Thermal-motion ellipsoids of 50% probability. (a) Molecule 1, (b) molecule 2, (c) molecule 3, (d) the bridging bonds, viewed as in Fig. 2(a).

CH₂-CH₂ bridges is indicated by the C-C distance of 1.571 ± 2 Å, compared with the standard value of 1.541 ± 3 Å (*International Tables for X-ray Crystallography*, 1962), and the C-C-C angles of 116 to 118°, compared with the strain-free tetrahedral value of 109.4°. This tension is balanced by compression of the nitrogen bridge, resulting in an average C-N-C angle of 99.4°. This is of course much smaller than the approximately tetrahedral value found for many secondary amines. (The C-N distance of 1.439 ± 2 Å may well differ from the equivalent strain-free value which is, however, unknown to the authors.) As indicated in Table 5, the phenyl rings show moderate boat distortion. If the 'prow' and 'stern' atoms are disregarded, the remaining four atoms of each ring are nearly coplanar. The dihedral angle between phenyl ring planes ranges from 93 to 95°.

The description so far is remarkably similar to that given for the less-accurately determined oxido analogue (Mathew & Hanson, 1968). Unlike this analogue, however, or the corresponding 1,9-diene (Hanson & Huml, 1969), the present molecule does not have even approximate *mm*2 symmetry. Each phenyl ring is twisted about its C-N bond by an angle which varies from 2.5 to 4.8°. In any molecule the twists are approximately equal, and have the same sense when viewed from N, so that approximate twofold symmetry is preserved. (Another measure of the twist is given by the angle between the bonds C(1)-C(2) and C(9)-C(10); this ranges from 10.4 to 17.2°.) The symmetry is necessarily violated by the amino hydrogen atom, which, because of the pyramidal configuration of bonds to the nitrogen atom, lies well off the twofold axis. It is thus brought into contact with one of the hydrogen atoms, [H(10a)] of the adjacent CH₂-CH₂ bridge. The H...H distance [*D* in Fig. 2(b)] varies from 2.26 to 2.29 Å, with an e.s.d. of about 0.07 Å. This distance is less than the sum of van der Waals radii (2.4 Å) and is thus *consistent* with (although insufficiently accurate to *prove*) steric repulsion. The hypothesis of repulsion is more convincingly demonstrated by the observed displacement of the nitrogen atom from the twofold axis, in a direction which increases the H...H distance. Because of this displacement, the angle between the plane containing C(8), N, C(16) and the mean plane of C(1), C(2), C(9), C(10) [*E* in Fig. 2(b)] is 92.3 to 93.4°, instead of the right angle which could otherwise be expected.

Fig. 2(b) demonstrates that one result of molecular twisting is the avoidance of the eclipsed conformation for the CH₂-CH₂ groups. The conformation angles of the individual bridging bonds (as determined by the adjacent C-C bonds) range from 8.8 to 18.5°, with a mean value of 13.6°. (As determined by appropriate pairs of C-H bonds, the mean conformation angle is 14°.) The energy advantage of avoiding the eclipsed conformation will be small (1 or 2 kcal. mole⁻¹) and will be partly offset by the resultant crowding of the imino hydrogen atom. Nevertheless, it seems sufficient

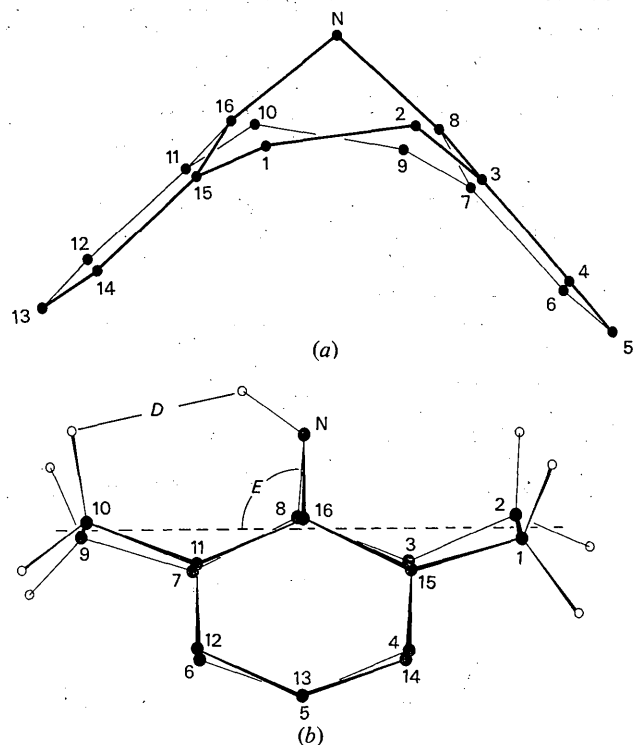


Fig. 2. Two views of molecule 2, showing the molecular twist. Where included, hydrogen atoms are shown as open circles.

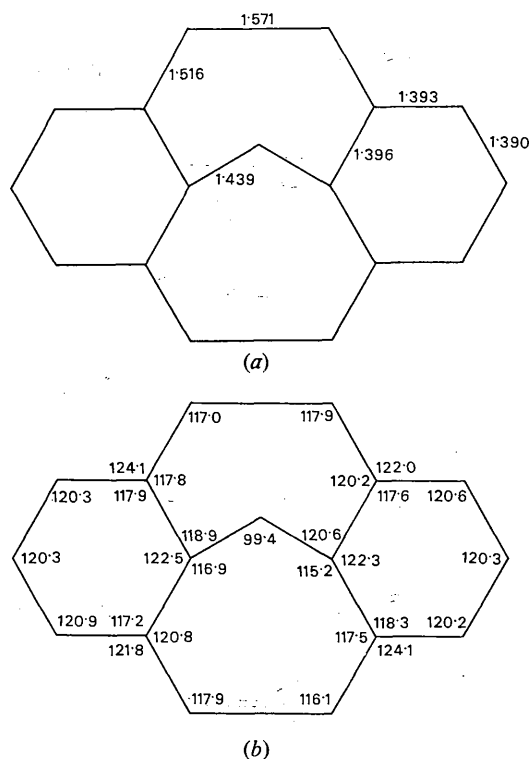


Fig. 3. (a) Mean bond lengths, in Å. (b) Mean bond angles, in degrees. (Note, however, that corresponding angles in different molecules are not strictly comparable.)

to stabilize the twisted conformation. Resistance to small changes in the degree of twist should be small also; this conclusion is consistent with the hypotheses, advanced earlier, that the varying degrees of twist observed for the several molecules are determined by packing forces, and that twisting modes are likely to be important in the description of the thermal motion.

The nuclear magnetic resonance spectrum of the material in solution is consistent with *mm2* symmetry. The molecule in this situation is presumably flipping between twisted conformations of opposite sense. Any interaction between the imino group and the protons of the bridging system is too small to detect (Boekelheide, 1969).

Table 4. *Angles (e.s.d.'s) in degrees for the three molecules 1, 2 and 3 and their mean values*

| Angle | 1 | 2 | 3 | Mean |
|--------------------------|-----------|---------------|-----------|-------|
| 15-1-2 | 117.8 (3) | 118.4 (3) | 117.6 (3) | 117.9 |
| 1-2-3 | 115.7 (3) | 115.6 (3) | 116.9 (3) | 116.1 |
| 7-9-10 | 118.2 (3) | 118.7 (3) | 117.9 (3) | 118.3 |
| 9-10-11 | 117.8 (3) | 116.8 (3) | 117.0 (3) | 117.2 |
| 2-3-8 | 117.9 (3) | 116.7 (3) | 117.9 (3) | 117.5 |
| 8-7-9 | 120.6 (3) | 119.9 (3) | 120.2 (3) | 120.2 |
| 10-11-16 | 118.0 (3) | 117.6 (3) | 117.8 (3) | 117.8 |
| 1-15-16 | 121.4 (3) | 121.3 (3) | 119.8 (3) | 120.8 |
| 2-3-4 | 124.3 (3) | 124.0 (3) | 123.9 (3) | 124.1 |
| 6-7-9 | 121.5 (3) | 122.6 (3) | 121.8 (3) | 122.0 |
| 10-11-12 | 124.2 (3) | 123.9 (3) | 124.2 (3) | 124.1 |
| 14-15-1 | 121.1 (3) | 121.4 (3) | 122.8 (3) | 121.8 |
| 8-3-4 | 117.7 (3) | 119.1 (3) | 118.1 (3) | 118.3 |
| 8-7-6 | 117.6 (3) | 117.4 (3) | 117.7 (3) | 117.6 |
| 16-11-12 | 117.6 (3) | 118.4 (3) | 117.8 (3) | 117.9 |
| 14-15-16 | 117.4 (3) | 117.1 (3) | 117.2 (3) | 117.2 |
| 3-4-5 | 120.4 (3) | 119.5 (3) | 120.8 (3) | 120.2 |
| 5-6-7 | 120.3 (3) | 120.8 (3) | 120.7 (3) | 120.6 |
| 11-12-13 | 120.4 (3) | 120.0 (3) | 120.4 (3) | 120.3 |
| 13-14-15 | 120.7 (3) | 120.7 (3) | 121.3 (3) | 120.9 |
| 3-8-N | 114.6 (3) | 115.9 (3) | 115.0 (3) | 115.2 |
| 7-8-N | 120.6 (3) | 120.4 (3) | 120.9 (3) | 120.6 |
| 11-16-N | 118.4 (3) | 119.0 (3) | 119.2 (3) | 118.9 |
| 15-16-N | 117.2 (3) | 116.9 (3) | 116.5 (3) | 116.9 |
| 4-5-6 | 120.6 (3) | 120.4 (3) | 120.0 (4) | 120.3 |
| 12-13-14 | 120.4 (3) | 120.4 (3) | 120.1 (3) | 120.3 |
| 3-8-7 | 122.8 (3) | 122.0 (3) | 122.0 (3) | 122.3 |
| 11-16-15 | 122.5 (3) | 122.4 (3) | 122.6 (3) | 122.5 |
| 8-N-16 | 100.1 (2) | 99.1 (2) | 98.9 (2) | 99.4 |
| Mean C-C-H (aromatic) | | 120 (116-124) | | |
| Mean C-C-H (tetrahedral) | | 108 (103-116) | | |
| Mean H-C-H | | 107 (99-114) | | |
| Mean C-N-H | | 109 (106-114) | | |

Table 5. *Summary of the molecular geometry*

| Molecule | A | B | C | D | E | F | G |
|----------|---------------|-------|-----------------|--------|-------|--------------------|--------------------|
| 1 | 3.9° (3.9) | 16.6° | 18.4° (12.6) | 2.29 Å | 92.7° | 0.112 Å (0.096) | 0.050 Å (0.028) |
| 2 | 4.5 (4.8) | 17.2 | 18.5 (12.4) | 2.26 | 92.3 | 0.109 (0.093) | 0.036 (0.047) |
| 3 | 2.5 (3.4) | 10.4 | 8.8 (10.8) | 2.26 | 93.4 | 0.090 (0.096) | 0.031 (0.032) |

- A. Twist about C-N bond of ring C(3)···C(8) (and of ring C(11)···C(16)). (*A* would be zero for a molecule with *mm2* symmetry.)
 B. Angle between C(1)-C(2) and C(9)-C(10).
 C. Conformation angle of C(1)-C(2) (and of C(9)-C(10)), as determined by adjacent C-C bonds.
 D. Distance H(N)···H(10a) [Fig. 2(b)].
 E. Angle between planes C(8), N, C(16) and C(1), C(2), C(9), C(10) [Fig. 2(b)].
 F. Distance of C(8) (and of C(16)) from the mean plane of the four nearest phenyl carbon atoms.
 G. Distance of C(5) (and of C(13)) from the mean plane of the four nearest phenyl carbon atoms.

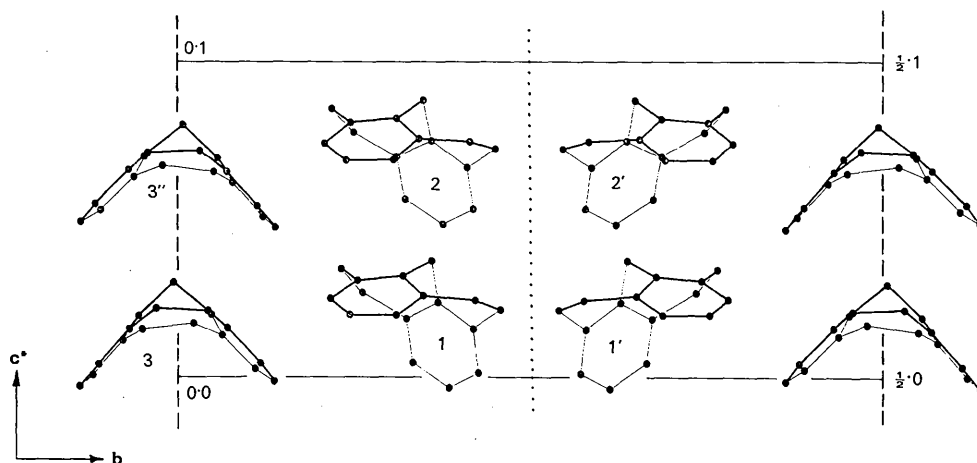


Fig. 4. A projection of the structure along *a*. Unprimed numbers refer to the molecules specified in Table 1. A single prime indicates the operation $\frac{1}{2} + x, \frac{1}{2} - y, z$, and a double prime, $x, \bar{y}, \frac{1}{2} + z$.

The reason proposed for the molecular twist should be even more cogent for the oxido analogue (II), which has no equivalent of the imino hydrogen atom to cause steric hindrance. Nevertheless, (II) is reported to have *mm*2 symmetry (Mathew & Hanson, 1968). However, the molecule makes use of a crystallographic mirror plane, and suffers intense thermal motion; the apparent symmetry may be descriptive only of the time- or space-average of a disordered structure in which the individual molecules are twisted. The reported phase change on cooling may indicate the transition to an ordered structure of lower symmetry.

The molecular packing is illustrated in Fig. 4. The shortest intermolecular contacts are: C-C, 3.39; C-N, 3.36; H-H, 2.44 Å. Study of the molecular packing suggests that the transition to the room-temperature structure may proceed as follows. As a result of thermal disorder the sequence of units in the chain of molecules related by the *c* glide plane (3,3'', 3,3''...) becomes random. The average molecule in the chain appears to be the superposition of 3 and 3'', and the *c* glide plane becomes a mirror plane. A very slight change in the position and orientation of molecules 1 and 2 makes the pseudo-translation (*c*/2) exact. The repeat distance in the *z* direction is halved, and the space group becomes *Cm*.

The problem was suggested, and the specimen material supplied, by Professor V. Boekelheide. Dr C. K. Johnson's (1965) *ORTEP* program was used for Fig. 1. All other computations were carried out using the programs of Ahmed, Hall, Pippy & Huber (1966); the block-diagonal least-squares program was modified by Dr Ahmed. The assistance of those named is gratefully acknowledged.

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