

Structure of 4-(Diethylamino)-1,10-ethano-5-methylcyclopentacyclononene

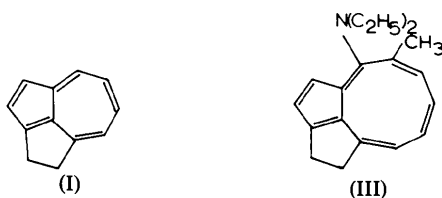
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Abstract. $C_{19}H_{23}N$, monoclinic, $P2_1/a$, $a = 20.88$ (1), $b = 8.667$ (5), $c = 8.991$ (5) Å, $\beta = 108.00$ (5)°, $Z = 4$, $D_c = 1.140$, $D_m = 1.13$ (1) Mg m⁻³, $\mu(Cu K\alpha) = 0.42$ mm⁻¹. The structure, which was refined to $R = 0.069$, reveals the conformation of the conjugated bicyclic cyclopentacyclononene.

Introduction. Like azulene and 4,6,8-trimethylazulene (Hafner, Lindner & Ude, 1979a; Lindner, Kitschke, Hafner & Ude, 1980), dihydrocyclopent[cd]azulene (I) undergoes cycloaddition with 1-(diethylamino)propyne (II) (Hafner, Lindner & Ude, 1979b). The additional ethano bridge in (I) should hinder or rule out valence isomerization of the nine-membered ring formed by the cycloaddition and allow the isolation of a substituted cyclopentacyclononene. The 1:1 adduct of (I) and (II) was found to have the structure (III) by crystal structure analysis.



Crystals of (III) were grown from ether as brownish-red prisms. The crystal system was determined from Weissenberg photographs. Intensities were collected on a Stoe two-circle diffractometer (Cu $K\alpha$ radiation) equipped with a graphite monochromator. The crystal was orientated along b . 2340 reflections, $h0l$ to $h6l$, with $\theta \leq 62.5^\circ$ were measured in the $\theta-2\theta$ scan mode. The data were corrected for background and for Lorentz and polarization factors, but not for absorption.

The structure was solved by direct methods and refined by full-matrix least squares with *SHELX 76* (Sheldrick, 1977). Anisotropic refinement of the C and N atoms and refinement of the positions of the H atoms using 1608 reflections with $|F| > 2\sigma$ reduced R to 0.069. The highest peak in the final difference map did not exceed 0.35 e Å⁻³.

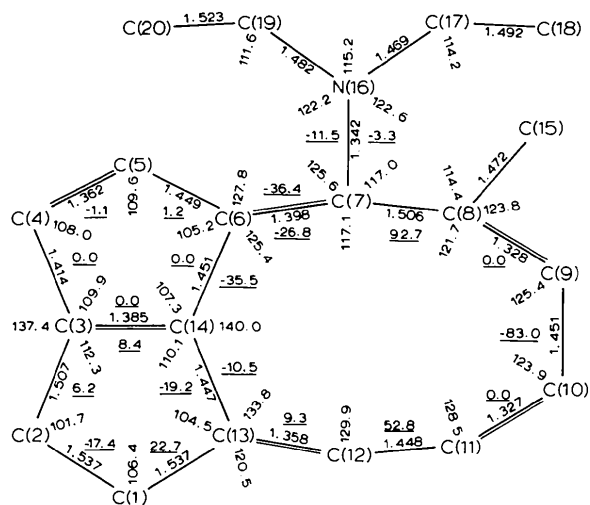


Fig. 1. Bond lengths (Å), bond angles (°) and some torsion angles (°) (underlined values) ($\sigma_{xx} = 0.005$ Å, $\sigma_{xxx} = 0.4^\circ$, $\sigma_{xxxx} = 0.8^\circ$; $x = C, N$).

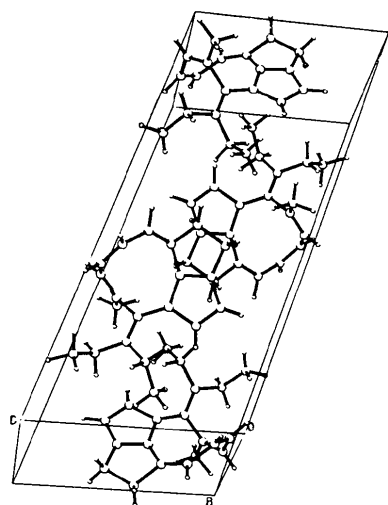


Fig. 2. The contents of the unit cell. View down b , with c horizontal and a vertical.

Table 1. *Positional parameters of the atoms with their e.s.d.'s in parentheses*

| | x | y | z |
|----------|------------|------------|------------|
| C(1) | 0.4798 (2) | 0.7414 (6) | 0.4106 (5) |
| C(2) | 0.5191 (2) | 0.7121 (7) | 0.5834 (5) |
| C(3) | 0.5851 (2) | 0.6517 (4) | 0.5722 (4) |
| C(4) | 0.6478 (2) | 0.6038 (5) | 0.6762 (4) |
| C(5) | 0.6912 (2) | 0.5832 (4) | 0.5917 (3) |
| C(6) | 0.6568 (1) | 0.6148 (4) | 0.4281 (3) |
| C(7) | 0.6778 (1) | 0.5769 (3) | 0.2992 (3) |
| C(8) | 0.6252 (1) | 0.5136 (4) | 0.1573 (3) |
| C(9) | 0.5905 (2) | 0.6046 (5) | 0.0416 (4) |
| C(10) | 0.5980 (2) | 0.7707 (6) | 0.0359 (4) |
| C(11) | 0.5681 (2) | 0.8704 (6) | 0.1050 (4) |
| C(12) | 0.5235 (2) | 0.8391 (5) | 0.1968 (4) |
| C(13) | 0.5322 (2) | 0.7450 (4) | 0.3224 (4) |
| C(14) | 0.5890 (1) | 0.6597 (4) | 0.4214 (3) |
| C(15) | 0.6130 (2) | 0.3467 (5) | 0.1639 (5) |
| N(16) | 0.7416 (1) | 0.5782 (3) | 0.2960 (3) |
| C(17) | 0.7612 (2) | 0.5139 (5) | 0.1653 (5) |
| C(18) | 0.7873 (3) | 0.6304 (8) | 0.0763 (6) |
| C(19) | 0.7971 (2) | 0.6484 (4) | 0.4227 (4) |
| C(20) | 0.8457 (2) | 0.5267 (5) | 0.5162 (5) |
| H(C1) | 0.455 (3) | 0.844 (5) | 0.397 (5) |
| H'(C1) | 0.449 (2) | 0.647 (6) | 0.371 (5) |
| H(C2) | 0.498 (2) | 0.633 (5) | 0.629 (5) |
| H'(C2) | 0.526 (2) | 0.807 (6) | 0.635 (5) |
| H(C4) | 0.655 (2) | 0.572 (5) | 0.790 (5) |
| H(C5) | 0.735 (2) | 0.532 (5) | 0.630 (5) |
| H(C9) | 0.560 (2) | 0.563 (5) | -0.046 (5) |
| H(C10) | 0.629 (2) | 0.830 (5) | -0.017 (5) |
| H(C11) | 0.570 (2) | 0.978 (6) | 0.088 (5) |
| H(C12) | 0.483 (2) | 0.904 (5) | 0.174 (5) |
| H(C15) | 0.650 (2) | 0.269 (6) | 0.189 (5) |
| H'(C15) | 0.583 (2) | 0.277 (5) | 0.054 (5) |
| H''(C15) | 0.595 (2) | 0.340 (5) | 0.252 (5) |
| H(C17) | 0.798 (2) | 0.428 (5) | 0.209 (5) |
| H'(C17) | 0.727 (2) | 0.449 (5) | 0.098 (5) |
| H(C18) | 0.793 (2) | 0.554 (5) | -0.033 (5) |
| H'(C18) | 0.827 (3) | 0.668 (5) | 0.121 (5) |
| H''(C18) | 0.754 (3) | 0.722 (5) | 0.047 (5) |
| H(C19) | 0.823 (3) | 0.721 (5) | 0.374 (5) |
| H'(C19) | 0.775 (2) | 0.714 (5) | 0.496 (5) |
| H(C20) | 0.884 (2) | 0.562 (5) | 0.594 (5) |
| H'(C20) | 0.868 (2) | 0.459 (5) | 0.454 (5) |
| H''(C20) | 0.824 (2) | 0.447 (5) | 0.560 (5) |

Discussion. Coordinates of the atoms are given in Table 1,* bond lengths, bond angles and some torsion angles in Fig. 1. Fig. 2 shows the packing of the molecules.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34926 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The conjugated system consists of a nearly planar 6-aminofulvene moiety with bond lengths typical for this delocalized π system (Ammon & Wheeler, 1971) and a non-planar polyene system in the nine-membered ring with double-bond fixation and high torsion angles of the single bonds (53, 83 and 93°). The weakening of the exocyclic fulvene double bond C(6)–C(7) is manifested by the rather long bond (1.398 Å) and the torsion angle C(5)–C(6)–C(7)–N(16) of 30°. The short C(7)–N(16) distance and the planarity of N(16) indicate a strong interaction between the lone electron pair of the N atom and the fulvene π system. The conformation of the nine-membered ring corresponds to that of 1-(dimethylcarbamoyl)azonine (Chiang, Paul, Anastassiou & Eachus, 1974) and is similar to the tub form of cyclooctatetraene. The strain introduced by the ethano bridge leads to bond-angle distortions at C(3), C(13) and C(14). The rigidity of this part of the molecule probably prevents the electrocyclic reaction between C(8) and C(13) which usually occurs in conjugated systems with nine-membered rings (Boche, Böhme & Martens, 1969; Boche, Weber, Martens & Bieberbach, 1978). The crystal packing (Fig. 2) does not show any interactions other than van der Waals.

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