The Structure of 2-Piperidinotricyclo[5.2.2.0^{2,6}]undecan-9-one*

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Abstract

$C_{16}H_{25}NO$, $M_r = 247 \cdot 3$, is monoclinic, *Cc*, with $a = 24 \cdot 28$ (4), $b = 8 \cdot 76$ (6), $c = 14 \cdot 03$ (2) Å, $\beta = 108 \cdot 00$ (9)°, $Z = 8$, $D_m = 1 \cdot 18$, $D_c = 1 \cdot 16$ Mg m^{-3}. The structure was determined to obtain accurate information about the geometry of the molecule as there was ambiguity in the chemical structure. The structure was refined to $R = 6 \cdot 3\%$ for 1165 visually measured reflections with two independent molecules in the asymmetric unit. The structure established by the X-ray method is completely different from that proposed on the basis of chemical and physical data. The new structure explains some reactions which could not be understood from the previously proposed structure.

Introduction

The structure of the title compound has been determined by an X-ray method as the structural information obtained by chemical and other physical methods gave rise to certain ambiguities.

The compound, obtained from Dr Balaji Rao (Banaras Hindu University, Varanasi, 1978), is formed by a novel reaction which has given rise to a new chemistry of enamines.

The structure established by the present X-ray study (Fig. 1) is completely different from that previously

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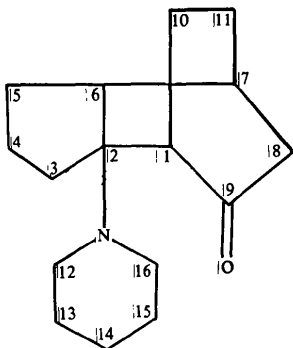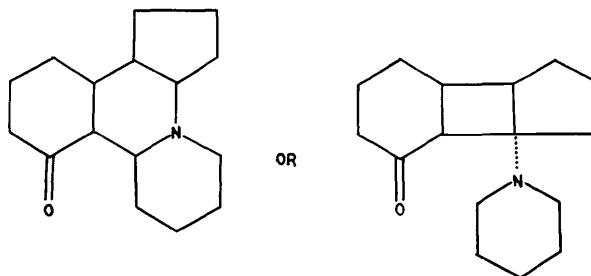

Fig. 2. Structures proposed by chemical and physical data.

proposed on the basis of chemical and physical evidence (Fig. 2).

Experimental

White glassy crystals were grown by evaporation from a hexane solution. Rotation and Weissenberg photographs of the crystal were taken at room temperature using Cu *Kα* radiation. Systematic absences on Weissenberg photographs indicated the monoclinic space groups *C2/c* or *Cc*.

Three-dimensional intensity data were collected using a Weissenberg camera and Ni-filtered Cu *Kα* radiation for layers $k = 0$ to 7 and $l = 0$ to 2, by mounting the crystal along the *b* and *c* axes respectively. The multiple-film equi-inclination Weissenberg technique (Robertson, 1943) was used for higher-layer data collection.

The intensities were estimated visually by comparison with a calibrated set of intensities and were corrected for Lorentz, polarization and spot-shape factors. Using 45 reflections common to both axes the two sets of data were correlated by the method of Rollett & Sparks (1960). Using the correlated layer scales, the data were brought to an approximately absolute scale by the Wilson (1942) method. The overall isotropic thermal parameter was $1 \cdot 75$ Å^2.

Determination of the structure

To resolve the space-group ambiguity, the distribution of the normalized structure amplitudes $|E|$ was

Fig. 1. Chemical formula.

calculated using the three-dimensional intensity data. The distribution favours the choice of Cc rather than $C2/c$. Though the distribution of intensities is non-centric we selected the centrosymmetric space group to start with because, according to density measurements, the number of molecules per unit cell is eight, which is the general-position multiplicity in $C2/c$. However, the refinement of the structure confirmed the space group Cc with two molecules in the asymmetric unit.

The structure was solved by the direct method using *MULTAN* (Germain, Main & Woolfson, 1971). 175 reflections with $|E| > 1·47$ were input to the program. Two linearly independent reflections, 174 and $9,3,\overline{11}$, with $|E|$ values 2·32 and 2·09 respectively, were chosen to define the origin for the centrosymmetric space group $C2/c$. In addition, three reflections, $9\overline{36}$, $\overline{646}$, $16,4,4$, were also selected as starting reflections in the multisolution approach. Among the multisolution sets, one with a Karle R factor of 21·7%, an ABSFOM of 1·55 and a combined figure of merit of 2·0 was chosen for an E map on which 14 non-hydrogen atoms could be identified. The molecular model based on these atoms did not correspond to the chemical structure given to us, although there were two rings common to the X-ray model and the proposed chemical structure. The difference map revealed the remaining non-hydrogen atoms, and the structure was found to be completely different from that proposed by chemical and other physical data. The molecule includes cyclopentane, piperidine and bicyclooctane fragments.

Structure factor calculations gave an R factor of 30% after three cycles of block-diagonal least-squares refinement of eight layer scale factors, together with positional and isotropic thermal parameters of the C, N and O atoms using the program written by Shiono (1968). Three more cycles of block-diagonal least-squares refinement with the Cruickshank (1956) weighting scheme brought the R factor down to 23·8%.

Three cycles of refinement of overall scale factor and positional and isotropic thermal parameters brought the R factor down to 19%. At this stage stereo-chemically reasonable positions of H atoms were calculated, and their inclusion in the structure factor calculation gave an R factor of 18%. Then the refinement was continued in the non-centrosymmetric space group Cc with two molecules in the asymmetric unit. Four cycles of refinement of overall scale factor, positional and anisotropic thermal parameters of 36 non-hydrogen atoms with calculated positional and assumed isotropic thermal parameters ($B_{iso} = 3·0$ Å²) of 50 H atoms gave an R value of 11·2%. Three more cycles of refinement with an absorption correction [μ(Cu $K\alpha$) = 5·7 cm⁻¹] reduced R to 6·3%. An approximate absorption correction (Palm, 1964) was made assuming the crystal to be cylindrical.

Table 1. *Final positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters for non-hydrogen atoms with e.s.d.'s*

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

	x	y	z	β_{eq} (Å²)
O(I,1)	2677 (3)	4137	2363 (5)	82 (6)
N(I,1)	3883 (2)	2527 (7)	4044 (4)	19 (5)
C(I,1)	2981 (3)	3874 (9)	4228 (6)	35 (6)
C(I,2)	3657 (3)	3550 (8)	4746 (5)	8 (5)
C(I,3)	3770 (3)	2531 (9)	5748 (6)	38 (7)
C(I,4)	4273 (4)	3232 (9)	6443 (6)	31 (7)
C(I,5)	4251 (3)	4928 (9)	6192 (7)	24 (7)
C(I,6)	4020 (4)	5010 (9)	5003 (7)	41 (8)
C(I,7)	3674 (3)	6354 (9)	4513 (6)	27 (7)
C(I,8)	3396 (4)	5795 (9)	3283 (6)	32 (7)
C(I,9)	3013 (3)	4605 (9)	3207 (6)	25 (6)
C(I,10)	2760 (4)	5106 (9)	4725 (9)	68 (10)
C(I,11)	3164 (5)	6735 (9)	4962 (9)	104 (13)
C(I,12)	4509 (3)	2075 (9)	4441 (6)	35 (7)
C(I,13)	4719 (4)	1460 (9)	3593 (8)	55 (9)
C(I,14)	4360 (4)	−63 (9)	3087 (9)	71 (9)
C(I,15)	3712 (3)	550 (9)	2685 (6)	26 (6)
C(I,16)	3530 (3)	1125 (9)	3711 (6)	44 (7)
O(II,2)	2270 (3)	−867 (9)	2665 (5)	88 (7)
N(II,2)	1121 (2)	−2509 (7)	969 (4)	20 (5)
C(II,1)	1963 (3)	−1151 (9)	905 (6)	22 (5)
C(II,2)	1332 (3)	−1683 (8)	288 (6)	16 (5)
C(II,3)	1284 (4)	−2267 (9)	−754 (6)	19 (7)
C(II,4)	712 (3)	−1479 (9)	−1505 (6)	40 (8)
C(II,5)	776 (4)	121 (9)	−1131 (7)	60 (9)
C(II,6)	962 (3)	−76 (8)	0 (6)	11 (5)
C(II,7)	1370 (4)	1272 (9)	596 (7)	39 (7)
C(II,8)	1595 (4)	1152 (9)	1612 (7)	69 (9)
C(II,9)	2003 (4)	−419 (9)	1809 (8)	33 (8)
C(II,10)	2199 (3)	45 (9)	252 (7)	40 (8)
C(II,11)	1907 (3)	1575 (9)	246 (6)	15 (6)
C(II,12)	517 (4)	−3000 (9)	597 (6)	32 (7)
C(II,13)	292 (3)	−3580 (9)	1424 (6)	34 (7)
C(II,14)	647 (3)	−4829 (9)	1960 (7)	26 (7)
C(II,15)	1331 (4)	−4575 (9)	2229 (8)	78 (10)
C(II,16)	1478 (3)	−3817 (9)	1491 (6)	24 (6)

The final positional and thermal parameters of the non-hydrogen atoms are listed in Table 1.*

Results and discussion

The compound studied is not soluble in hydrochloric acid. This is fully explained by the molecular structure, in which the N lone pair is not available for protonation because of steric overcrowding. The Grignard reaction does not proceed due to the developing negative charge interacting with the N lone pair.

The bond lengths and angles involving non-hydrogen atoms averaged over molecules (I) and (II) of the asymmetric unit are given in Figs. 3 and 4. Chemically equivalent bond lengths in molecules (I) and (II) are only slightly different. The standard deviations in the bond lengths and angles are about 0·016 Å and 1·1° respectively.

The mean $C(sp^3)-C(sp^3)$ distance, 1·56 (2) Å, is normal. The average value of C(1)–C(9) and C(8)–C(9) is 1·50 (1) Å and is in agreement with the standard value of 1·506 Å for the $C(sp^3)-C(sp^2)$ single bond (Lide, 1962).

The average C–N distance, 1·48 (2) Å, is in agreement with the $C(sp^3)-N(sp^3)$ single-bond length (1·48 Å).

The observed C=O bond length of 1·26 (2) Å agrees with the value of 1·252 Å proposed by Marsh & Donohue (1967). The least-squares plane through O,
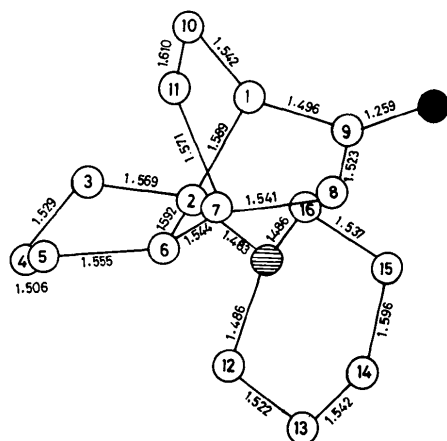

Fig. 5. Projection of the asymmetric unit along [010].

Fig. 3. Bond lengths (Å) (e.s.d. 0·009–0·016 Å).

Table 2. *Intermolecular distances* ($<4·0$ Å) *with e.s.d.'s*

Symmetry code: (i) $x, y, \frac{1}{2} + z$; (ii) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

O(I,1)···C(II,15)	3·40 (2)	C(II,8)···C(II,4ⁱ)	3·89 (1)
O(I,1)···C(II,16)	3·31 (1)	C(II,3)···C(II,15ⁱ)	3·98 (2)
C(I,8)···O(II,2)	3·91 (1)	C(II,4)···C(II,14ⁱ)	3·86 (1)
C(I,9)···C(II,15)	3·95 (2)	C(I,3)···C(I,15ⁱ)	3·86 (1)
C(I,11)···O(II,2)	3·89 (2)	O(I,1)···C(I,10ⁱ)	3·82 (2)
C(II,8)···C(II,15)	3·93 (2)	O(I,1)···C(I,11ⁱ)	3·97 (2)
C(I,8)···C(I,4ⁱ)	3·91 (1)	C(I,4)···C(II,4ⁱⁱ)	3·78 (2)
C(I,10)···C(II,11ⁱ)	3·77 (1)	C(I,13)···C(II,13ⁱⁱ)	3·71 (2)
C(I,11)···C(II,10ⁱ)	3·76 (2)	C(I,13)···C(II,14ⁱⁱ)	3·84 (2)
C(I,11)···C(II,11ⁱ)	3·52 (1)	C(I,14)···C(II,13ⁱⁱ)	3·94 (1)
C(I,3)···C(II,14ⁱ)	3·81 (2)	C(I,14)···C(II,14ⁱⁱ)	3·92 (1)
C(I,4)···C(II,14ⁱ)	3·57 (1)	C(I,13)···C(II,5ⁱⁱⁱ)	3·88 (2)
O(II,2)···C(II,10ⁱ)	3·75 (2)		

C(9), C(1) and C(8) shows that these atoms are quite coplanar.

The molecular structure is shown in Fig. 5. Molecules (I) and (II) in the asymmetric unit are approximately centrosymmetrically related. There are no short intermolecular contacts (Table 2) and the molecules are loosely packed. In fact, the density of the crystal is as low as 1·16 Mg m⁻³. The crystal structure on the whole is completely stabilized by van der Waals interactions.

Fig. 4. Bond angles (°) (e.s.d. 0·5–1·1°). C(1)–C(2)–N 107·5, C(3)–C(2)–N 113·1, C(6)–C(2)–N 109·2°.

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The Structure of 2,3,8,8a-Tetrahydro-5,8a-diphenyl-1*H*-imidazo[2,1-*c*][1,4]thiazine

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Abstract

The title compound $C_{18}H_{18}N_2S$ is monoclinic with unit-cell dimensions $a = 7.4729$ (11), $b = 23.5631$ (10), $c = 8.7006$ (14) Å, $\beta = 104.965$ (16)°. The space group is $P2_1/c$ with $Z = 4$, $d_m = 1.31$, $d_c = 1.323$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 1.71$ cm⁻¹. The structure was solved by direct methods. A full-matrix least-squares refinement based on 1909 reflections with $F \geq 3\sigma(F)$ converged to give $R = 0.0669$ and $R_w = 0.058$. All non-H atoms were refined anisotropically. H atoms were located on geometrical considerations and during refinement they were kept isotropic. $S-C(sp^2)$ and $S-C(sp^3)$ distances are 1.747 (4) and 1.796 (5) Å respectively. The C—S—C bond angle is 97.8 (2)° and the average C—C bond distance in the phenyl rings is 1.392 Å.

Introduction

The condensation reaction of 2,2′-thiodiacetophenone (I) with 1,2-diaminopropane (II) proceeds *via* the formation of thiadiazonine (III), which on transannular interaction of the N atom with C=N results in the formation of the imidazo[2,1-*c*][1,4]thiazine system (IV). This has been established with the help of ¹³C NMR spectral studies on a series of products isolated from a number of similar reactions (Sandhu, Tandon & Singh, 1980). The formation of a bicyclic product has been confirmed by crystal-structure determination (Sandhu & Hundal, 1982) of the product where $R = CH_3$. However, when the same reaction is carried out with 1,2-diaminoethane, $R = H$, the ¹³C spectra of the

product indicated the presence of a thiadiazonine ring system. An X-ray diffraction study of this product was considered essential to provide unequivocal evidence for or against the formation of a thiadiazonine ring system.

$$R = CH_3 \text{ or } H$$
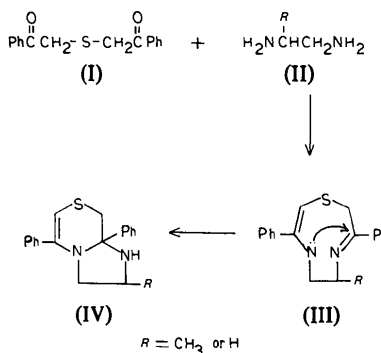
Experimental

Colourless prismatic crystals of the compound under consideration were grown from ethyl acetate solution by slow evaporation. Preliminary space-group information was obtained from the Weissenberg photographs. The final accurate unit-cell parameters and intensity data were determined on a CAD-4 diffractometer.

Reflections were scanned in the ω–2θ mode with ω scan width $(0.85 + 0.35 \tan \theta)°$. The maximum scan time for each reflection was 60 s. Two standard reflections (410 and 204) were measured at regular intervals to provide a check on crystal and electronic stability. The variations observed in the intensities did not necessitate any corrective measures. 3193 reflections within the range $1.5 < \theta < 25°$ were collected.

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