

1,3-Diphenylspiro[imidazolidine-2,2'-indan]-1',3'-dione

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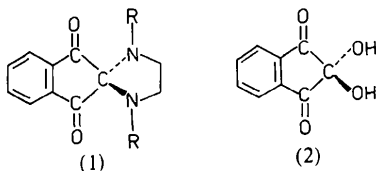
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Abstract. $C_{23}H_{18}N_2O_2$, triclinic, $P\bar{1}$, $a = 9.225$ (4), $b = 12.982$ (5), $c = 8.286$ (2) Å, $\alpha = 102.11$ (2), $\beta = 108.93$ (4), $\gamma = 95.53$ (3)°, $M_r = 354.4$, $Z = 2$, $D_x = 1.30$ Mg m⁻³; $R = 0.047$ for 2394 reflections. The title compound contains neither an approximate twofold rotation axis nor an approximate mirror plane. One of the N atoms displays a trigonal-planar the other a pyramidal coordination geometry. The tetrahedral geometry of the spiro C atom is significantly flattened.

Introduction. Ninhydrin (2) reacts with *N,N'*-disubstituted ethylenediamines to yield 1,4-diazaspiro[4.4]-nonanes ($R = C_2H_5$, C_6H_5 , *m*- $CH_3C_6H_4$, *p*- $CH_3C_6H_4$, *p*- $CH_3OC_6H_4$), which exhibit a characteristic deep-red colouration (Schönberg, Singer, Osch & Hoyer, 1975; Schönberg, Singer, Eschenhof & Hoyer, 1978). The magnetic equivalence of the *R* groups and the appearance of the NCH_2CH_2N bridge as a sharp singlet in the ¹H NMR spectra indicate that these molecules must display a twofold symmetry axis or a plane of symmetry in solution. As their colour and long-wavelength UV bands cannot be explained in terms of classical chromophore theory, it was decided to determine the X-ray structure of one derivative, namely (1) with $R = C_6H_5$.



Cell dimensions were determined by a least-squares fit to the 2θ settings for $15 \pm (hkl)$ reflections on a Syntex $P2_1$ diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å). Data collection was carried out in the θ - 2θ mode ($2\theta \leq 135^\circ$). No absorption correction was

deemed necessary [$\mu(Cu K\alpha) = 0.59$ mm⁻¹]. The crystal was of prismatic habit with dimensions $0.42 \times 0.23 \times 0.37$ mm. After application of the observation criterion $F_o^2 \geq 2.0\sigma(F_o^2)$, 2394 independent reflections (from 3224 recorded) were retained for use in the analysis. The structure was solved by direct methods with *SHELX* (Sheldrick, 1976) and refined by full-matrix least squares with anisotropic temperature factors for the non-hydrogen atoms. The H-atom positional parameters were refined freely with individual temperature factors. Terminal values for *R* and

Table 1. Positional parameters ($\times 10^4$) and equivalent isotropic temperature factors ($\text{Å}^2 \times 10^3$) for the non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	2942 (2)	3861 (1)	6987 (3)	45 (1)
C(2)	2935 (2)	3037 (2)	7955 (3)	45 (1)
C(3)	1538 (2)	2142 (1)	6814 (3)	41 (1)
C(4)	566 (2)	2672 (2)	5437 (3)	46 (1)
C(5)	1569 (2)	3657 (2)	5537 (3)	48 (1)
N(6)	752 (2)	1653 (1)	7777 (2)	52 (1)
C(7)	1009 (3)	562 (2)	7735 (3)	55 (1)
C(8)	2356 (3)	516 (2)	7100 (3)	57 (1)
N(9)	2046 (2)	1219 (1)	5903 (2)	44 (1)
C(10)	4096 (3)	4735 (2)	7345 (3)	61 (1)
C(11)	3839 (3)	5393 (2)	6227 (4)	74 (1)
C(12)	2472 (4)	5198 (2)	4789 (4)	79 (1)
C(13)	1315 (3)	4331 (2)	4415 (3)	66 (1)
O(2)	3865 (2)	3035 (1)	9378 (2)	66 (1)
O(4)	-762 (2)	2327 (1)	4462 (2)	66 (1)
C(61)	-204 (2)	2129 (2)	8568 (3)	49 (1)
C(62)	-322 (3)	3206 (2)	8750 (3)	60 (1)
C(63)	-1325 (3)	3642 (2)	9514 (3)	73 (1)
C(64)	-2205 (3)	3025 (3)	10143 (3)	81 (1)
C(65)	-2071 (3)	1975 (3)	10002 (3)	78 (1)
C(66)	-1103 (3)	1514 (2)	9221 (3)	63 (1)
C(91)	3137 (2)	1424 (1)	5061 (3)	44 (1)
C(92)	2592 (2)	1629 (2)	3414 (3)	52 (1)
C(93)	3613 (3)	1829 (2)	2563 (3)	62 (1)
C(94)	5172 (3)	1810 (2)	3337 (4)	67 (1)
C(95)	5709 (3)	1596 (2)	4955 (3)	68 (1)
C(96)	4700 (3)	1400 (2)	5821 (3)	57 (1)

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Table 2. Hydrogen-atom positional parameters ($\times 10^3$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	x	y	z	U
H(71)	8 (2)	6 (2)	693 (3)	72 (6)
H(72)	128 (2)	44 (2)	897 (3)	68 (6)
H(81)	340 (2)	79 (2)	812 (3)	71 (6)
H(82)	236 (2)	-19 (2)	641 (3)	73 (6)
H(10)	508 (2)	485 (2)	837 (3)	79 (7)
H(11)	471 (3)	607 (2)	647 (3)	105 (8)
H(12)	230 (3)	567 (2)	397 (3)	97 (8)
H(13)	36 (2)	419 (2)	342 (3)	76 (7)
H(62)	34 (2)	367 (2)	833 (3)	67 (6)
H(63)	-136 (3)	442 (2)	953 (3)	97 (8)
H(64)	-292 (3)	335 (2)	1070 (3)	107 (8)
H(65)	-271 (3)	154 (2)	1053 (3)	120 (10)
H(66)	-103 (3)	71 (2)	906 (3)	90 (7)
H(92)	146 (2)	164 (1)	287 (2)	55 (5)
H(93)	319 (2)	199 (2)	141 (3)	87 (7)
H(94)	594 (2)	197 (2)	275 (3)	88 (7)
H(95)	687 (3)	163 (2)	556 (3)	101 (8)
H(96)	511 (2)	124 (2)	697 (3)	78 (7)

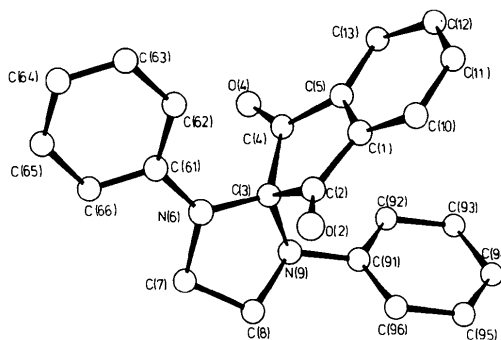


Fig. 1. Molecular structure of (1).

coordinates, with equivalent isotropic temperature factors $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ (Willis & Pryor, 1975) for the non-hydrogen atoms. Table 3 gives the bond distances and Table 4 the bond angles. Fig. 1 was drawn by *RSPLIT* (Sheldrick, 1975).

Table 3. Selected bond lengths (\AA)

C(1)–C(2)	1.466 (3)	C(1)–C(5)	1.390 (2)
C(2)–C(3)	1.537 (2)	C(2)–O(2)	1.213 (2)
C(3)–C(4)	1.537 (3)	C(3)–N(6)	1.438 (3)
C(3)–N(9)	1.477 (3)	C(4)–C(5)	1.475 (3)
C(4)–O(4)	1.206 (2)	N(6)–C(7)	1.453 (3)
N(6)–C(61)	1.378 (3)	C(7)–C(8)	1.500 (4)
C(8)–N(9)	1.465 (3)	N(9)–C(91)	1.433 (3)

Table 4. Selected bond angles ($^\circ$)

C(5)–C(1)–C(2)	110.1 (2)	C(1)–C(2)–C(3)	107.4 (1)
O(2)–C(1)–C(1)	127.2 (2)	O(2)–C(2)–C(3)	125.3 (2)
C(4)–C(3)–C(2)	102.9 (2)	N(6)–C(3)–C(2)	115.1 (2)
N(6)–C(3)–C(4)	117.1 (2)	N(9)–C(3)–C(2)	111.0 (2)
N(9)–C(3)–C(4)	109.1 (2)	N(9)–C(3)–N(6)	101.8 (2)
C(5)–C(4)–C(3)	107.1 (1)	O(4)–C(4)–C(3)	125.5 (2)
O(4)–C(4)–C(5)	127.5 (2)	C(4)–C(5)–C(1)	110.2 (2)
C(61)–N(6)–C(3)	124.6 (2)	C(61)–N(6)–C(7)	123.4 (2)
C(7)–N(6)–C(3)	111.9 (2)	C(8)–C(7)–N(6)	102.4 (2)
N(9)–C(8)–C(7)	101.5 (2)	C(8)–N(9)–C(3)	105.5 (2)
C(91)–N(9)–C(3)	118.3 (2)	C(91)–N(9)–C(8)	118.9 (2)

R_w were, respectively, 0.047 and 0.046. The generalized R factor $R_g = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$ was 0.049. Weights were given by $w = k[\sigma^2(F_o) + 0.0002F_o^2]^{-1}$. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). * Tables 1 and 2 lists the final atomic

* Lists of structure factors, anisotropic thermal parameters and all bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36512 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. In the crystalline state, (1) contains neither an approximate twofold rotation axis nor an approximate mirror plane. This is illustrated, in particular, by the coordination geometries observed at N(6) and N(9).

Whereas the coordination geometry of N(6) is trigonal planar (sum of the valence angles = 359.9°), that of N(9) is markedly pyramidal (sum of the valence angles = 342.7°). The endo- and exocyclic bond angles at N(6) are between 4.5 and 6.4° wider than the equivalent bond angles at N(9). As a result of this very marked coordination difference, the bond distances of 1.438 (2) and 1.378 (3) \AA for N(6)–C(3) and N(6)–C(61) are significantly shorter than those of 1.477 (3) and 1.433 (3) \AA , respectively, for N(9)–C(3) and N(9)–C(91). This suggests a considerable degree of π delocalization over the bond N(6)–C(61) but not over N(9)–C(91), which is supported by the fact that the phenyl ring at N(6) makes an angle of only 8.3° with the least-squares plane through C(3), C(7), C(61) and N(6), whereas an angle of 55.7° is observed for the phenyl ring at N(9) with the least-squares plane through C(3), C(8), C(91) and N(9). The five-membered ring CN(Ph)CH₂CH₂N(Ph)C is puckered at C(8). Distances from the least-squares plane through the remaining four atoms are as follows: C(3) 0.054, N(6) -0.057, C(7) 0.036, C(8) 0.584, N(9) -0.033 \AA .

The asymmetry of the bonding at C(3) is also reflected in its coordination, which displays a marked distortion from a tetrahedral geometry in the direction of a trigonal-planar geometry. This distortion may best be documented by a comparison of the sum of the three bond angles ($=\alpha_j$) at C(3), which do not involve N(9), with the sum of those which do not involve N(6). These are, respectively, 335.1 and 322.0° . For an idealized tetrahedral geometry this sum should be 328.4° . If we express the degree of distortion Δ_i as $\Delta_i = \sum_{j=1}^2 |\alpha_j -$

328.41/2(360 – 328.4)] \times 100% then we find a value of 21% for C(3). The non-bonded distances from O(2) and O(4) to the N atoms N(6) and N(9) are similar: O(2)···N(6) 2.96 (1), O(4)···N(6) 3.00 (1), O(2)···N(9) 3.15 (1), O(4)···N(9) 3.10 (1) Å. The observed flattening of the tetrahedron and the shortness of the bond C(3)–N(6) suggest that the hybridization at C(3) must contain a degree of sp^2 character.

The asymmetry of molecule (1) is not observable on the NMR time scale. It is interesting to note, in this context, that an analogous asymmetry is observed at C(3) in the structure of the parent compound ninhydrin (2) (Medrud, 1969). This was not commented upon in the original paper. One of the exocyclic C(3)–O bonds is 1.414 (5) Å, the other being significantly shorter at 1.360 (7) Å. An analogous flattening of the tetrahedron at C(3) to that in (1) is also observed. The possibility of ninhydrin being stabilized by zwitterionic resonance contributions was proposed almost 40 years ago (Schönberg & Moubacher, 1943). The present results combined with those for ninhydrin do indeed lend support to such resonance contributions and suggest that the observed UV spectra of (1)

and analogous derivatives may be a result of a partial involvement of C(3) in the chromophoric system.

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Structure of Pentacyclo[7.4.2.0^{2,6}.0^{6,15}.0^{11,14}]pentadec-4-ene-7,13-dione, a Novel Pentacyclic C₁₅ Quinane System

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Abstract. C₁₅H₁₆O₂ (a synthetic precursor to dodecahedrane), monoclinic, $P2_1/n$, $a = 12.171$ (5), $b = 6.976$ (5), $c = 13.868$ (3) Å, $\beta = 102.56$ (3)°, $Z = 4$, $D_m = 1.30$, $D_c = 1.318$ g cm⁻³, $F(000) = 488$, $\mu(\text{Mo } K\alpha) = 0.92$ cm⁻¹. Intensity data were collected on a Nonius CAD-4 diffractometer and the structure was solved by direct methods. Full-matrix least-squares refinement gave $R = 0.077$ ($R_w = 0.076$) for 1337 observed reflections. All the five-membered rings are *cis* fused and have envelope (C_s symmetry) conformations.

Introduction. In recent years much effort has been concentrated upon the synthetic methodology of polyquinanes because of their occurrence in a number of natural products and their fascinating topologies (Paquette, 1979). The title compound (Fig. 1) has a C₁₅ pentacyclic frame with a C₁₂ tetraquinane moiety (Mehta, Rao, Bhadbhade & Venkatesan, 1981). Crystals were grown by slow evaporation from methanol. The unit cell was found to be monoclinic and systematic absences indicated the space group $P2_1/n$. Accurate unit-cell parameters were obtained by least-squares analysis of θ values for 19 reflections using a Nonius CAD-4 diffractometer. A crystal of dimensions 0.2 \times 0.5 \times 0.3 mm was used and a total of 2017

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