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Structures of Diazapolycyclic Compounds.

VII. 1,4-Diphenyl-1,4-dihydrobenzo[*g*]pyridazino[1,2-*b*]phthalazine-6,13-dione and 1,4-Dihydrobenzo[*g*]pyridazino[1,2-*b*]phthalazine-6,13-dione

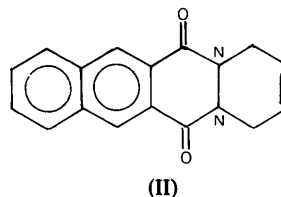
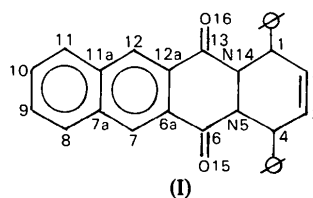
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Abstract

Crystal data: (I) $C_{28}H_{20}N_2O_2$, $M_r = 416.48$, $C2/c$, $a = 20.2629$ (5), $b = 7.3456$ (1), $c = 28.9414$ (20) Å, $\beta = 106.77$ (1)°, $V = 4124.5$ (4) Å³, $Z = 8$, $D_x = 1.34$ Mg m⁻³; (II) $C_{16}H_{12}N_2O_2$, $M_r = 264.28$, $P2_12_12_1$, $a = 24.2169$ (10), $b = 12.5360$ (40), $c = 3.9942$ (1) Å, $V = 1212.6$ (4) Å³, $Z = 4$, $D_x = 1.45$ Mg m⁻³. The structures have been solved by direct methods and refined by least-squares procedures. Final R values are 0.044 ($R_w = 0.051$) and 0.039 ($R_w = 0.048$) for 2738 and 1092 observed reflections for I and II respectively. The geometries of the two compounds were compared by half-normal probability plots, the pyridazine rings presenting different conformations.



Introduction

This work belongs to a series of studies designed to clarify some possible pharmacological activity in analogues of tetracyclines (Apreada, Foces-Foces, Cano & García-Blanco, 1980). It was undertaken to investigate the possible modification, from compound II to I, of the pyridazine ring, due to the presence of substituents.

Experimental and refinement methods

Experimental data and structure solution parameters are summarized in Table 1 together with the refinement procedures. Figs 1(a) and 1(b) display *ORTEP* drawings (Johnson, 1965) with the atomic numbering. In Tables 2 and 3 are shown the coordinates for I and II respectively. The bond distances and angles are listed in Tables 4 and 5. Some torsion angles are given in

Table 1. *Experimental data and structure refinement parameters*

	I	II
Unit cell determination	Least squares fit from 95 54 reflexions with $\theta < 45^\circ$	
Crystal size (mm)	0.45 × 0.11 × 0.29 0.35 × 0.07 × 0.07	
Stability	No significant variation	
Technique and geometry	Four circle diffractometer (Philips PW 1100) with graphite monochromated radiation: $\omega/2\theta$ scan mode	
Radiation	Cu $K\alpha$	
μ (mm ⁻¹)	0.6376	0.7496
Total measurement, up to θ (°)	65	65
Number of independent reflexions	3287	1267
Criterion for observed reflexions	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Number of observed reflexions	2738	1092
Atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974)	
Computer programs	XRAY 70 system (Stewart, Kundell & Baldwin, 1970)	
Solution	MULTAN 78 system (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978)	
Refinement method	Block diagonal on observed F^2 's	
H atoms	From difference synthesis	
Parameters refined	(coordinates and anisotropic temperature factors)	
Non hydrogen atoms	288	180
Hydrogen atoms	(coordinates and isotropic temperature factors)	
Extinction correction	80	48
Number of reflexions per parameter	7	5
Weighting scheme	Empirical fit so as to give no trends in $\langle w\Delta^2F \rangle$ vs $\langle F_o \rangle$ or $\langle \sin \theta/\lambda \rangle$	
Final electron density (e Å ⁻³)	0.10	0.12

Table 2. *Atomic parameters for C₂₈H₂₀N₂O₂*

$$U_{eq} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* a_i a_j \cos(a_i a_j) \text{ \AA}^2 \times 10^4.$$

Thermal parameters for H as $\exp[-8\pi^2 U(\sin \theta/\lambda)^2] \text{ \AA}^2 \times 10^3.$

	x	y	z	U_{eq}/U
C(1)	0.24546 (10)	0.3051 (3)	-0.11081 (7)	443 (6)
C(1E)	0.23448 (9)	0.1735 (3)	-0.15304 (6)	438 (6)
C(2E)	0.17527 (12)	0.1746 (4)	-0.19109 (8)	619 (8)
C(3E)	0.16952 (16)	0.0612 (4)	-0.23052 (10)	764 (10)
C(4E)	0.22261 (16)	-0.0519 (4)	-0.23213 (10)	738 (11)
C(5E)	0.28186 (16)	-0.0512 (4)	-0.19481 (10)	723 (10)
C(6E)	0.28787 (12)	0.0609 (3)	-0.15543 (8)	598 (8)
C(2)	0.24826 (11)	0.4935 (3)	-0.12926 (7)	533 (7)
C(3)	0.20415 (12)	0.6219 (3)	-0.12876 (8)	586 (8)
C(4)	0.14669 (12)	0.6002 (3)	-0.10651 (7)	526 (7)
C(1F)	0.07677 (11)	0.6070 (3)	-0.14365 (7)	565 (7)
C(2F)	0.05203 (20)	0.7771 (5)	-0.16161 (10)	897 (13)
C(3F)	-0.01047 (29)	0.7916 (8)	-0.19499 (14)	1233 (20)
C(4F)	-0.05080 (19)	0.6402 (9)	-0.21113 (12)	1201 (20)
C(5F)	-0.02645 (15)	0.4708 (7)	-0.19370 (11)	972 (14)
C(6F)	0.03780 (12)	0.4548 (4)	-0.15972 (9)	694 (9)
N(5)	0.15600 (8)	0.4386 (2)	-0.07541 (5)	454 (5)
C(6)	0.11551 (10)	0.4328 (2)	-0.04466 (6)	444 (6)
C(6a)	0.11621 (9)	0.2645 (2)	-0.01726 (6)	406 (5)
C(7)	0.07673 (10)	0.2534 (3)	-0.01411 (6)	429 (6)
C(7a)	0.07514 (9)	0.0916 (2)	0.03978 (6)	417 (6)
C(8)	0.03473 (11)	0.0754 (3)	0.07236 (7)	508 (7)
C(9)	0.03390 (12)	-0.0837 (3)	0.09598 (8)	571 (7)
C(10)	0.07217 (11)	-0.2358 (3)	0.08880 (7)	540 (7)
C(11)	0.11224 (11)	-0.2245 (3)	0.05825 (7)	479 (6)
C(11a)	0.11504 (9)	-0.0606 (2)	0.03304 (6)	415 (5)
C(12)	0.15586 (10)	-0.0443 (3)	0.00120 (6)	422 (6)
C(12a)	0.15591 (9)	0.1148 (2)	-0.02387 (6)	402 (5)
C(13)	0.19837 (9)	0.1282 (2)	-0.05733 (6)	426 (6)
N(14)	0.19168 (8)	0.28246 (19)	-0.08529 (5)	429 (5)
O(15)	0.08001 (8)	0.56509 (18)	-0.04182 (5)	592 (5)
O(16)	0.23846 (8)	0.00796 (19)	-0.06140 (5)	580 (5)
H(1)	0.2906 (11)	0.268 (3)	-0.0862 (7)	16 (5)
H(2E)	0.1411 (15)	0.259 (4)	-0.1914 (9)	42 (7)
H(3E)	0.1293 (18)	0.071 (5)	-0.2560 (13)	62 (9)
H(4E)	0.2194 (15)	-0.133 (4)	-0.2600 (12)	59 (8)
H(5E)	0.3188 (20)	-0.136 (5)	-0.1963 (13)	76 (10)
H(6E)	0.3299 (14)	0.055 (4)	-0.1279 (10)	52 (7)
H(2)	0.2853 (13)	0.512 (3)	-0.1448 (9)	35 (6)
H(3)	0.2071 (14)	0.739 (4)	-0.1420 (10)	49 (7)
H(4)	0.1494 (13)	0.702 (4)	-0.0842 (10)	42 (7)
H(2F)	0.0817 (28)	0.896 (8)	-0.1494 (20)	130 (18)
H(3F)	-0.0299 (27)	0.915 (8)	-0.2089 (19)	120 (16)
H(4F)	-0.0918 (20)	0.665 (6)	-0.2341 (14)	92 (12)
H(5F)	-0.0486 (20)	0.360 (5)	-0.2030 (13)	73 (11)
H(6F)	0.0547 (15)	0.333 (4)	-0.1470 (11)	53 (8)
H(7)	0.0501 (12)	0.354 (3)	0.0176 (8)	23 (5)
H(8)	0.0095 (14)	0.179 (4)	0.0767 (9)	37 (6)
H(9)	0.0078 (14)	-0.095 (4)	0.1187 (10)	41 (6)
H(10)	0.0687 (13)	-0.350 (4)	0.1049 (9)	41 (6)
H(11)	0.1382 (12)	-0.322 (3)	0.0536 (8)	25 (5)
H(12)	0.1834 (11)	-0.146 (3)	-0.0031 (7)	19 (5)

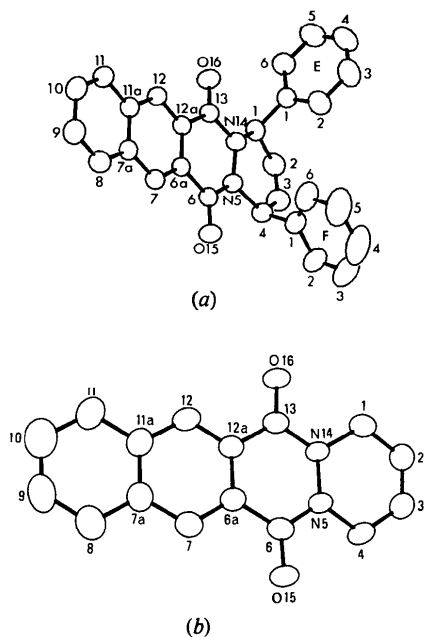


Fig. 1. ORTEP drawing of (a) I and (b) II showing the atomic numbering.

Table 6. Conformational parameters for the pyridazine rings are given in Tables 7 and 8.*

Discussion

Compounds I and II have been compared by half-normal probability plots (Abrahams & Keve, 1971);

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36949 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Atomic parameters for C₁₆H₁₂N₂O₂

$$U_{eq} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* a_i a_j \cos(a_i a_j) \text{ \AA}^2 \times 10^4.$$

Thermal parameters for H as $\exp[-8\pi^2 U(\sin \theta/\lambda)^2] \text{ \AA}^2 \times 10^3.$

	x	y	z	U _{eq} /U
C(4)	0.24334 (14)	0.13715 (22)	-0.1457 (11)	550 (11)
C(3)	0.20128 (13)	0.21272 (24)	-0.2574 (10)	565 (10)
C(2)	0.20601 (12)	0.31686 (24)	-0.2113 (10)	554 (11)
C(1)	0.25385 (13)	0.36673 (21)	-0.0509 (10)	543 (11)
N(14)	0.29595 (9)	0.29236 (16)	0.0742 (7)	437 (7)
C(13)	0.33998 (11)	0.33647 (19)	0.2300 (9)	459 (9)
C(12a)	0.38755 (11)	0.26737 (19)	0.3010 (7)	414 (8)
C(12)	0.43296 (12)	0.30759 (22)	0.4637 (8)	473 (9)
C(11a)	0.47974 (11)	0.24405 (23)	0.5252 (8)	463 (9)
C(11)	0.52731 (14)	0.28404 (30)	0.6853 (9)	600 (12)
C(10)	0.57164 (14)	0.21867 (34)	0.7429 (10)	674 (13)
C(9)	0.57105 (15)	0.11253 (33)	0.6445 (10)	665 (13)
C(8)	0.52637 (13)	0.07121 (30)	0.4850 (10)	604 (11)
C(7a)	0.47874 (11)	0.13533 (22)	0.4186 (8)	471 (9)
C(7)	0.43194 (12)	0.09583 (21)	0.2536 (8)	472 (9)
C(6a)	0.38714 (11)	0.15984 (19)	0.1919 (8)	407 (8)
C(6)	0.33853 (11)	0.11688 (19)	0.0215 (8)	433 (8)
N(5)	0.29576 (9)	0.18483 (15)	-0.0412 (7)	440 (7)
O(16)	0.33914 (9)	0.43226 (14)	0.3044 (7)	626 (8)
O(15)	0.33455 (8)	0.02239 (13)	-0.0633 (7)	575 (7)
H(4A)	0.249 (2)	0.089 (3)	-0.317 (11)	52 (12)
H(4B)	0.229 (2)	0.086 (4)	0.043 (13)	67 (14)
H(3)	0.168 (1)	0.183 (3)	-0.351 (10)	35 (9)
H(2)	0.181 (1)	0.364 (3)	-0.312 (10)	38 (10)
H(1A)	0.244 (2)	0.412 (3)	0.144 (11)	53 (12)
H(1B)	0.277 (2)	0.416 (3)	-0.223 (12)	64 (13)
H(12)	0.434 (1)	0.386 (2)	0.528 (9)	27 (8)
H(11)	0.529 (1)	0.355 (3)	0.733 (11)	40 (10)
H(10)	0.601 (2)	0.248 (3)	0.840 (10)	46 (12)
H(9)	0.604 (1)	0.070 (3)	0.684 (10)	47 (11)
H(8)	0.522 (2)	-0.001 (3)	0.415 (12)	54 (12)
H(7)	0.431 (1)	0.021 (3)	0.168 (9)	31 (9)

Table 4. Bond distances (Å) for C₂₈H₂₀N₂O₂ (I) and C₁₆H₁₂N₂O₂ (II)

	I	II	I	II
C(1)—C(1E)	1.523 (3)	—	C(9)—C(10)	1.409 (3)
C(1)—C(2)	1.490 (3)	1.464 (5)	C(10)—C(11)	1.365 (3)
C(1)—N(14)	1.492 (3)	1.469 (4)	C(11)—C(11a)	1.417 (3)
C(1E)—C(2E)	1.375 (3)	—	C(11a)—C(12)	1.410 (3)
C(1E)—C(6E)	1.379 (3)	—	C(12)—C(12a)	1.375 (3)
C(2E)—C(3E)	1.391 (4)	—	C(12a)—C(13)	1.472 (3)
C(3E)—C(4E)	1.371 (5)	—	C(13)—N(14)	1.376 (2)
C(4E)—C(5E)	1.364 (4)	—	C(13)—O(16)	1.229 (2)
C(5E)—C(6E)	1.383 (4)	—		1.237 (3)
C(2)—C(3)	1.302 (3)	1.323 (4)	C(1)—H(1)	1.02 (2)
C(3)—C(4)	1.493 (4)	1.461 (5)	C(2E)—H(2E)	0.93 (3)
C(4)—C(1F)	1.512 (3)	—	C(3E)—H(3E)	0.93 (3)
C(4)—N(5)	1.469 (2)	1.464 (4)	C(4E)—H(4E)	0.99 (3)
C(1F)—C(2F)	1.390 (4)	—	C(5E)—H(5E)	0.98 (4)
C(1F)—C(6F)	1.370 (3)	—	C(6E)—H(6E)	0.99 (2)
C(2F)—C(3F)	1.357 (6)	—	C(2)—H(2)	0.99 (3)
C(3F)—C(4F)	1.379 (8)	—	C(3)—H(3)	0.95 (3)
C(4F)—C(5F)	1.379 (8)	—	C(4)—H(4)	0.98 (3)
C(5F)—C(6F)	1.392 (3)	—	C(2F)—H(2F)	1.06 (6)
N(5)—C(6)	1.374 (3)	1.364 (3)	C(3F)—H(3F)	1.02 (5)
N(5)—N(14)	1.428 (2)	1.425 (3)	C(4F)—H(4F)	0.92 (4)
C(6)—C(6a)	1.467 (2)	1.462 (4)	C(5F)—H(5F)	0.93 (4)
C(6)—O(15)	1.226 (2)	1.236 (3)	C(6F)—H(6F)	0.99 (3)
C(6a)—C(7)	1.375 (3)	1.372 (4)	C(7)—H(7)	0.94 (3)
C(6a)—C(12a)	1.407 (3)	1.417 (4)	C(8)—H(8)	0.95 (3)
C(7)—C(7a)	1.406 (3)	1.402 (4)	C(9)—H(9)	0.96 (3)
C(7a)—C(8)	1.421 (3)	1.431 (4)	C(10)—H(10)	0.97 (3)
C(7a)—C(11a)	1.426 (3)	1.428 (4)	C(11)—H(11)	0.92 (3)
C(8)—C(9)	1.357 (3)	1.358 (5)	C(12)—H(12)	0.96 (2)
			C(1)—H(1A)	—
			C(1)—H(1B)	—
			C(4)—H(4A)	—
			C(4)—H(4B)	—

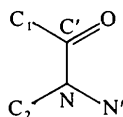
Table 5. Bond angles (°) for the heavy atoms for C₂₈H₂₀N₂O₂ (I) and C₁₆H₁₂N₂O₂ (II)

	I	II	I	II
C(2)—C(1)—N(14)	112.9 (2)	115.3 (3)	N(5)—C(6)—O(15)	119.4 (2)
C(1E)—C(1)—N(14)	111.6 (2)	—	N(5)—C(6)—C(6a)	117.5 (2)
C(1E)—C(1)—C(2)	108.3 (2)	—	C(6a)—C(6)—O(15)	123.1 (2)
C(1)—C(1E)—C(6E)	119.1 (2)	—	C(6)—C(6a)—C(12a)	120.1 (2)
C(1)—C(1E)—C(2E)	122.0 (2)	—	C(6)—C(6a)—C(7)	119.4 (2)
C(2E)—C(1E)—C(6E)	118.6 (2)	—	C(7)—C(6a)—C(12a)	120.5 (2)
C(1E)—C(2E)—C(3E)	120.1 (2)	—	C(6a)—C(7)—C(7a)	120.4 (2)
C(2E)—C(3E)—C(4E)	120.7 (2)	—	C(7)—C(7a)—C(11a)	119.3 (2)
C(3E)—C(4E)—C(5E)	119.4 (3)	—	C(7)—C(7a)—C(8)	121.8 (2)
C(4E)—C(5E)—C(6E)	120.2 (3)	—	C(8)—C(7a)—C(11a)	118.9 (2)
C(1E)—C(6E)—C(5E)	121.0 (2)	—	C(7a)—C(8)—C(9)	120.0 (2)
C(1)—C(2)—C(3)	124.8 (2)	123.4 (3)	C(8)—C(9)—C(10)	121.4 (2)
C(2)—C(3)—C(4)	123.4 (2)	122.5 (3)	C(9)—C(10)—C(11)	120.2 (2)
C(3)—C(4)—N(5)	111.9 (2)	115.3 (3)	C(10)—C(11)—C(11a)	120.3 (2)
C(3)—C(4)—C(1F)	112.2 (2)	—	C(7a)—C(11a)—C(11)	119.2 (2)
C(1F)—C(4)—N(5)	113.0 (2)	—	C(11)—C(11a)—C(12)	121.8 (2)
C(4)—C(1F)—C(6F)	123.0 (2)	—	C(7a)—C(11a)—C(12)	119.0 (2)
C(4)—C(1F)—C(2F)	117.3 (2)	—	C(11a)—C(12)—C(12a)	120.5 (2)
C(2F)—C(1F)—C(6F)	119.7 (2)	—	C(6a)—C(12a)—C(12)	120.3 (2)
C(1F)—C(2F)—C(3F)	119.9 (4)	—	C(12)—C(12a)—C(13)	119.6 (2)
C(2F)—C(3F)—C(4F)	121.2 (5)	—	C(6a)—C(12a)—C(13)	120.2 (2)
C(3F)—C(4F)—C(5F)	119.3 (4)	—	C(12a)—C(13)—O(16)	122.9 (2)
C(4F)—C(5F)—C(6F)	119.9 (4)	—	C(12a)—C(13)—N(14)	117.7 (2)
C(5F)—C(6F)—C(1F)	120.1 (3)	—	N(14)—C(13)—O(16)	119.4 (2)
C(4)—N(5)—N(14)	120.6 (2)	118.8 (2)	N(5)—N(14)—C(13)	120.9 (2)
C(4)—N(5)—C(6)	115.3 (2)	117.1 (2)	C(1)—N(14)—C(13)	114.9 (2)
C(6)—N(5)—N(14)	122.5 (2)	121.9 (2)	C(1)—N(14)—N(5)	119.6 (1)

Table 6. Torsion angles ($^{\circ}$) for the (a) pyridazine and (b) diazaquinonic rings

(a)	I	II
C(1)–C(2)–C(3)–C(4)	4.0 (4)	1.2 (5)
C(2)–C(3)–C(4)–N(5)	14.2 (3)	–3.1 (5)
C(3)–C(4)–N(5)–N(14)	–29.7 (2)	16.5 (4)
(φ_0) C(4)–N(5)–N(14)–C(1)	27.7 (2)	–23.1 (4)
N(5)–N(14)–C(1)–C(2)	–8.1 (2)	25.0 (4)
N(14)–C(1)–C(2)–C(3)	–7.6 (3)	–11.8 (5)
(b)	I	II
C(13)–N(14)–N(5)–C(6)	–13.1 (2)	5.2 (4)
N(14)–N(5)–C(6)–C(6a)	7.1 (2)	–4.3 (4)
N(5)–C(6)–C(6a)–C(12a)	–1.6 (3)	3.0 (4)
C(6)–C(6a)–C(12a)–C(13)	1.7 (3)	–2.5 (4)
C(6a)–C(12a)–C(13)–N(14)	–7.1 (2)	3.2 (4)
C(12a)–C(13)–N(14)–N(5)	12.5 (2)	–4.4 (4)

Table 7. Distortion parameters for the 'amide groups' around N(5) and N(14)



$$\omega_1 = \omega(C_1C'NC_2), \omega_2 = \omega(OC'NN'), \omega_3 = \omega(OC'NC_2), \\ \omega_4 = \omega(C_1C'NN')$$

$$\chi_N = \omega_2 - \omega_3 + \pi = -\omega_1 + \omega_4 + \pi \pmod{2\pi}$$

$$\chi_C = \omega_1 - \omega_3 + \pi = -\omega_2 + \omega_4 + \pi \pmod{2\pi}$$

χ_N and χ_C are parameters which describe the deviations from planarity of the 'amide group' in the nitrogen and carbon atoms respectively; τ is a measure of the mean torsion around the C–N bond; ω_i are the torsion angles around the C–N bond.

	N(5)		N(14)	
	I	II	I	II
χ_N ($^{\circ}$)	14.7 (2)	16.9 (3)	24.3 (2)	15.7 (3)
χ_C ($^{\circ}$)	–1.2 (2)	–0.8 (3)	0.7 (2)	–0.6 (3)
τ ($^{\circ}$)	180.4 (2)	176.3 (2)	180.1 (2)	176.8 (3)
N ($^{\circ}$)	119.4 (2)	119.3 (2)	118.5 (2)	119.4 (2)

Table 8. Conformational parameters ($^{\circ}$) for the pyridazine rings

φ_0 is the torsion angle around the N(5)–N(14) bond.

$$(-1)^j \tau_j = \tau_m + q \cos [(\Sigma/2) + (2\pi/6)j] \quad 6\tau_m = (\varphi_0 - \varphi_3) + (\varphi_4 - \varphi_1) + (\varphi_2 - \varphi_5) \quad \tan \frac{\Sigma}{2} = \frac{1}{\sqrt{3}} \frac{(\varphi_1 - \varphi_3) + (\varphi_4 - \varphi_2)}{(\varphi_0 + \varphi_3)}$$

$$q^2 = \frac{1}{4}(\varphi_0 + \varphi_3)^2 + \frac{1}{12}[(\varphi_1 - \varphi_3) + (\varphi_4 - \varphi_2)]^2 \quad \alpha_1 = (\Sigma + \delta)/2, \alpha_2 = (\Sigma - \delta)/2.$$

τ_m is the mean torsion in the ring; q is the amplitude of pseudorotation in the ring; α_1, α_2 are pseudorotation phases; Σ is the sum of α_1 and α_2 ; δ is the difference between α_1 and α_2 .

	Experimental		Theoretical			
	I	II	Envelope C(1)–C(2), C(2)–C(3)	Diplanar C(1)–C(2), C(3)–C(4)	Diplanar N(14)–C(1), C(3)–C(4)	Boat N(14)–C(1), C(3)–C(4)
τ_m ($^{\circ}$)	11.4 (3)	13.9 (5)	$\frac{\sqrt{3}}{2} q$	$q/2$	$q/2$	0
q ($^{\circ}$)	20.2 (2)	15.5 (1)	q	q	q	q
Σ ($^{\circ}$)	70.6 (2)	37.4 (1)	60	0	120	60
δ ($^{\circ}$)	112.1 (4)	52.5 (2)	60	120	120	180
α_1 ($^{\circ}$)	94.4 (2)	45.0 (1)	30	60	120	120
α_2 ($^{\circ}$)	–17.8 (2)	–7.6 (1)	0	–60	0	–60

the distance C(1)–C(4) (atoms where the phenyl rings are located in compound I) shows the only significant difference.

From the torsion angles of the pyridazine rings (see Table 6), we have calculated the distortion parameters for the 'amide groups' (Winkler & Dunitz, 1971) around the N(5)–C(6) and C(13)–N(14) bonds. The deformation with respect to sp^2 hybridization is, as usual, greater at nitrogen than at carbon (see Table 7).

The conformations of the pyridazine rings have been described according to a model for flexible six-membered rings (Cano, Foces-Foces & García-Blanco, 1977) (see Table 8). For I, the conformation is midway between the four conformations shown in Table 8 and for II the corresponding ring conformation is a distorted envelope at the C(1)–C(2) and C(2)–C(3) bonds.

In compound II, the diazaquinonic ring is more planar than in I. The attached O atoms, O(15) and O(16), have deviations of –0.080 (3) and 0.072 (3) Å in II and mean deviations of 0.071 (2) and –0.182 (2) Å in I from the plane through the ring.

The angle between the phenyl planes is, on average, 52.7 (2) $^{\circ}$.

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Structure of Bis(5-propylphenazinium)–Tris[2,2'-(2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile)], (NPP)₂(TCNQ)₃

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Abstract

The title compound, (C₁₅H₁₅N₂)₂(C₁₂H₄N₄)₃, (NPP)₂(TCNQ)₃, $M_r = 1059.18$, $d_c = 1.44 \text{ Mg m}^{-3}$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.913(2)$, $b = 12.187(4)$, $c = 13.262(4) \text{ \AA}$, $\alpha = 96.21(2)$, $\beta = 108.13(2)$, $\gamma = 97.36(2)^\circ$, $V = 1340.90 \text{ \AA}^3$ and $Z = 1$. All the molecules are planar with the exception of one TCNQ molecule, in which the planes through the =C(CN)₂ groups are slightly inclined with respect to the ring plane. Mixed stacks of NPP dimers and TCNQ trimers occur along the [011] direction. Final refinement yielded $R = 0.099$ and $R_w = 0.068$ for 1351 reflections. The EPR spectra consist of orientation-dependent structured triplet exciton lines.

Introduction

Phenazine, 5-alkylphenazinium salts and the 5-mono- or 5,10-dialkylated, 5,10-dihydrophenazines as donors form a wide variety of charge-transfer solids with the acceptor 2,2'-(2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile)(7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ). They differ in stoichiometry and/or in the molecular arrangement of the donors and the acceptors in the crystal lattice. With 1:1 composition typical *DADA* mixed stacks [as in phenazine (*P*)–TCNQ (Goldberg & Shmueli, 1973*a*), 5,10-dihydro-5,10-dimethylphenazine (Me₂P)–TCNQ (Goldberg & Shmueli, 1973*b*), Me₂P–TCNQF₄ (Soos, Keller,

Ludolf, Queckbörner, Wehe & Flandrois, 1981) and in 5-ethylphenazine(NEP)–TCNQ with σ -bonded and 'chain-linking' (TCNQ)₂²⁻ units (Morosin, Plastas, Coleman & Stewart, 1978; Harms, Keller, Nöthe, Werner, Gundel, Sixl, Soos & Metzger, 1981)], and π -overlapping dimerized structures with *DDAA* columns [as in 5-(1-butyl)phenazinium–TCNQF₄ (Metzger, Heimer, Gundel, Sixl, Harms, Keller, Nöthe & Wehe, 1982)] occur. Segregated regular stacks [as in the famous 5-methylphenazine (NMP)–TCNQ (Fritchie, 1966; Kobayashi, 1975) or in the phenazine-doped NEP–TCNQ, Me₂P–TCNQ and 5,10-dihydro-5,10-diethylphenazine (Et₂P)–TCNQ species (Sandman, 1978; Endres, Keller, Moroni & Wehe, 1980; Dietz, Endres, Keller, Moroni & Wehe, 1982)] can be found in 1:1 salts, too.

Only a few solids deviating from a 1:1 composition have been reported (Sanz & Daly, 1975; Dietz, Endres, Keller & Moroni, 1981; Harms, 1980), one of them [(NMP)₂(TCNQ)₃] with a complicated 2:3 lattice (Sanz & Daly, 1975). The latter compound is unique in this series, so far. Herein we report the preparation, X-ray and EPR data of (NPP)₂(TCNQ)₃, a compound with a lattice very similar to that of (NMP)₂(TCNQ)₃ but with surprising triplet exciton spectra.

Experimental

Chemical preparation

Crystals of (NPP)₂(TCNQ)₃ were grown by mixing hot solutions of (NPP)ClO₄ (100 mg) in absolute