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Structure of 1-(4-Nitrophenyl)pyrrole, -imidazole, -pyrazole and -1,2,4-triazole Derivatives

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Abstract. Structures of seven related compounds were determined to assess the nonlinear optical properties of the crystals. Mo $K\alpha$, $\lambda = 0.71073$ Å. 2-Methyl-1-(4-nitrophenyl)imidazole (I), $C_{10}H_9N_3O_2$, $M_r = 203.2$, monoclinic, $P2_1/c$, $a = 17.513$ (3), $b = 7.405$ (1), $c = 16.819$ (3) Å, $\beta = 118.25$ (1)°, $V = 1921.4$ (6) Å^3, $Z = 8$, $D_x = 1.40$ Mg m^{-3}, Mo $K\alpha$, $\mu = 0.095$ mm^{-1}, $F(000) = 848$, $T = 300$ (1) K, $R = 0.049$ for 2172 reflections. 2,4-Dimethyl-1-(4-nitrophenyl)imidazole (II), $C_{11}H_{11}N_3O_2$, $M_r = 217.2$, orthorhombic, $P2_1ab$, $a = 11.808$ (3), $b = 22.132$ (7), $c = 3.999$ (1) Å, $V = 1045.1$ (5) Å^3, $Z = 4$, $D_x = 1.38$ Mg m^{-3}, Mo $K\alpha$, $\mu = 0.092$ mm^{-1}, $F(000) = 456$, $T = 297$ (1) K, $R = 0.064$ for 723 reflections. 2-Ethyl-1-(4-nitrophenyl)imidazole (III), $C_{11}H_{11}N_3O_2$, $M_r = 217.2$, orthorhombic, $Pca2_1$, $a = 24.159$ (5), $b = 4.033$ (1), $c = 10.658$ (2) Å, $V = 1038.4$ (4) Å^3, $Z = 4$, $D_m = 1.38$ (1), $D_x = 1.39$ Mg m^{-3}, $\mu = 0.093$ mm^{-1}, $F(000) = 456$, $T = 300$ (1) K, $R = 0.043$ for 926 reflections. 1-(4-Nitrophenyl)-2-phenylimidazole (IV), $C_{15}H_{11}N_3O_2$, $M_r = 265.3$, triclinic, $P\bar{1}$, $a = 9.350$ (2), $b = 11.893$ (3), $c = 12.658$ (3) Å, $\alpha = 103.73$ (2), $\beta = 103.68$ (2), $\gamma = 97.05$ (2)°, $V = 1304.6$ (6) Å^3, $Z = 4$, $D_x = 1.35$ Mg m^{-3}, Mo $K\alpha$, $\mu = 0.087$ mm^{-1}, $F(000) = 552$, $T = 297$ (1) K, $R = 0.043$ for 1804 reflections. 1-(4-Nitrophenyl)pyrazole (V), $C_9H_7N_3O_2$, $M_r = 189.2$, monoclinic, $P2_1/n$, $a = 11.519$ (2), $b = 10.342$ (2), $c = 7.077$ (1) Å, $\beta = 93.68$ (1)°, $V = 841.3$ (2) Å^3, $Z = 4$, $D_m = 1.49$ (1), $D_x = 1.49$ Mg m^{-3}, Mo $K\alpha$, $\mu = 0.103$ mm^{-1}, $F(000) = 392$, $T = 299$ (1) K, $R = 0.045$ for 1188 reflections. 3,5-Dichloro-1-(4-nitrophenyl)-1,2,4-triazole (VI), $C_8H_4N_4O_2Cl_2$, $M_r = 259.1$, monoclinic, $P2_1$, $a = 11.282$ (4), $b = 11.902$ (5), $c = 3.753$ (1) Å, $\beta = 92.81$ (3)°, $V = 503.3$ (3) Å^3, $Z = 2$, $D_x =$

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1.71 Mg m^{-3}, Mo $K\alpha$, $\mu = 0.632$ mm^{-1}, $F(000) = 260$, $T = 297$ (1) K, $R = 0.023$ for 639 reflections. 1-(4-Nitrophenyl)pyrrole (VII), $C_{10}H_8N_2O_2$, $M_r = 188.2$, orthorhombic, $Fdd2$, $a = 13.651$ (2), $b = 10.930$ (2), $c = 11.721$ (2) Å, $V = 1748.8$ (5) Å^3, $Z = 8$, $D_m = 1.42$ (1), $D_x = 1.43$ Mg m^{-3}, Mo $K\alpha$, $\mu = 0.096$ mm^{-1}, $F(000) = 784$, $T = 301$ (1) K, $R = 0.044$ for 342 reflections. The nitro groups are almost in the plane of the benzene rings with dihedral angles of less than 14°. On the other hand, the five-membered hetero rings make angles of more than 36° to the benzene rings [except for (V): 2.5 (3)° and (VII): 15.1 (4)°] reflecting the steric repulsion between the hetero ring substituent proximal to the junction and the phenyl group. The molecular arrangements of (II) and (III) are essentially identical and are in a zigzag mode. When there is no substituent on the five-membered hetero ring, the molecules are packed with the long axes parallel (VII) or anti-parallel (V) to each other. Crystals of (VII) are expected to exhibit good nonlinear optical properties.

Experimental. The compounds were prepared by reacting azoles with 4-fluoronitrobenzene. The synthetic procedure for 1-(4-nitrophenyl)pyrrole is provided as a typical example: pyrrole 0.67 g (10 mmol), 4-fluoronitrobenzene 1.41 g (10 mmol) and potassium carbonate 1.38 g (10 mmol) were heated with 5 ml of *N*,*N*-dimethylformamide for 4 h at 363 K with stirring. The reaction mixture was poured onto 50 ml ice water and the precipitate collected by filtration. The precipitate was washed with water, dried and recrystallized twice from 2-propanol. Yield 1.21 g (64.4%), elemental analysis C 64.05 (calc. 63.82), H 4.17 (4.28), and N 14.89 (14.89%). The D_m values were measured by flotation in aqueous potassium iodide. X-ray intensities were measured on a Rigaku *AFC*-5 four-circle diffractometer at room temperature with Mo $K\alpha$ radiation monochromatized by a graphite plate. Cell constants were refined based on 18–36 reflections ($20 < 2\theta < 30°$). Five standard reflections showed no decay for all crystals. Criterion for observed reflections is $|F_o| > 3\sigma(|F_o|)$. Analytical absorption corrections were made except for (IV) and (VII). Structures were solved by direct methods with the program *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Non-H atoms were refined with anisotropic thermal parameters. Almost all H atoms were located in difference syntheses and the remaining atoms were calculated theoretically. H atoms were refined with isotropic thermal parameters. The function $\sum w(|F_o| - |F_c|)^2$ was minimized with weight $w^{-1} = \sigma^2(|F_o| + (0.015|F_o|)^2$. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were performed using the *UNICS*III program system (Sakurai & Kobayashi, 1979) on a FACOM M-380R computer of Keio University. Final atomic parameters are listed in Table 1. Crystal structures of (II), (III), (V), and (VII) are shown in Fig. 1.* Experimental details are as follows. (I): Colorless prisms elongated along *b* by sublimation in vacuum at 453 K, 0.50 × 0.40 × 0.40 mm. h $-21\rightarrow21$, k $0\rightarrow9$, l $0\rightarrow22$ ($2\theta \leq 55°$), θ–2θ scan, 4548 reflections measured, 2260 observed, 2172 unique (relative transmission factors $0.947 < A < 0.970$, $R_{\rm int} = 0.010$). Space group was determined to be $P2_1/c$ from systematic absences, $h0l$, l odd and $0k0$, k odd. The structure was difficult to solve because the two independent molecules are arranged with a pseudo translation of $a/2$ and of $c/2$. The Monte Carlo method for initial phase angles (Furusaki, 1979) was successful. Final $R = 0.049$, $wR = 0.051$, $S = 1.84$, $(\Delta/\sigma)_{\rm max} = 0.14$, $-0.32 < \Delta\rho < 0.22$ e Å^{-3}. (II): Pale-yellow hexagonal prisms elongated along *c* by sublimation, 0.30 × 0.30 × 0.50 mm. The ω-scan technique was adopted because of the relatively large peak half-width, 0.2 ~ 0.3°. h $-12\rightarrow12$, k $-23\rightarrow23$, l $0\rightarrow4$ ($2\theta \leq 45°$), 2625 reflections measured, 1763 observed, 723 unique ($0.970 < A < 0.984$, $R_{\rm int} = 0.028$). Laue group *mmm* with systematic absences $h0l$, h odd and $hk0$, k odd suggested the space group $P2_1ab$ (cab setting of $Pca2_1$) or $Pmab$ ($\bar{c}ba$ setting of $Pbcm$). Since $Z = 4$ and the molecules cannot lie on any set of special positions without disorder, the space group was determined to be $P2_1ab$. $R = 0.064$, $wR = 0.071$, $S = 3.44$, $(\Delta/\sigma)_{\rm max} = 0.20$, $-0.33 < \Delta\rho < 0.23$ e Å^{-3}. (III): Pale-yellow plate-like crystal (100) elongated along *b* from an acetone solution, 0.25 × 0.45 × 0.50 mm. h $0\rightarrow33$, k $0\rightarrow14$, l $0\rightarrow5$ ($2\theta \leq 60°$), peak half-width of 0.12 ~ 0.25°, ω scan, 1593 reflections measured, 926 observed unique reflections ($0.961 < A < 0.979$). Systematic absences $0kl$, l odd and $h0l$, h odd suggested the space group $Pca2_1$ or $Pcam$ ($ba\bar{c}$ setting of $Pbcm$). Since $Z = 4$ with no molecular symmetry, the space group was determined to be $Pca2_1$. $R = 0.043$, $wR = 0.039$, $S = 1.36$, $(\Delta/\sigma)_{\rm max} = 0.32$, $-0.28 < \Delta\rho < 0.16$ e Å^{-3}. (IV): Colorless prisms elongated along *a* by sublimation, 0.40 × 0.20 × 0.15 mm. h $-11\rightarrow11$, k $-14\rightarrow14$, l $0\rightarrow15$ ($2\theta \leq 50°$), θ–2θ scan, 4800 reflections measured, 1911 observed, 1804 unique (no absorption correction, $R_{\rm int} = 0.017$). Since $Z = 4$ for $P\bar{1}$, there are two independent molecules in the asymmetric unit. $R = 0.43$, $wR = 0.039$, $S = 1.25$, $(\Delta/\sigma)_{\rm max} = 0.30$, $-0.16 < \Delta\rho < 0.15$ e Å^{-3}.

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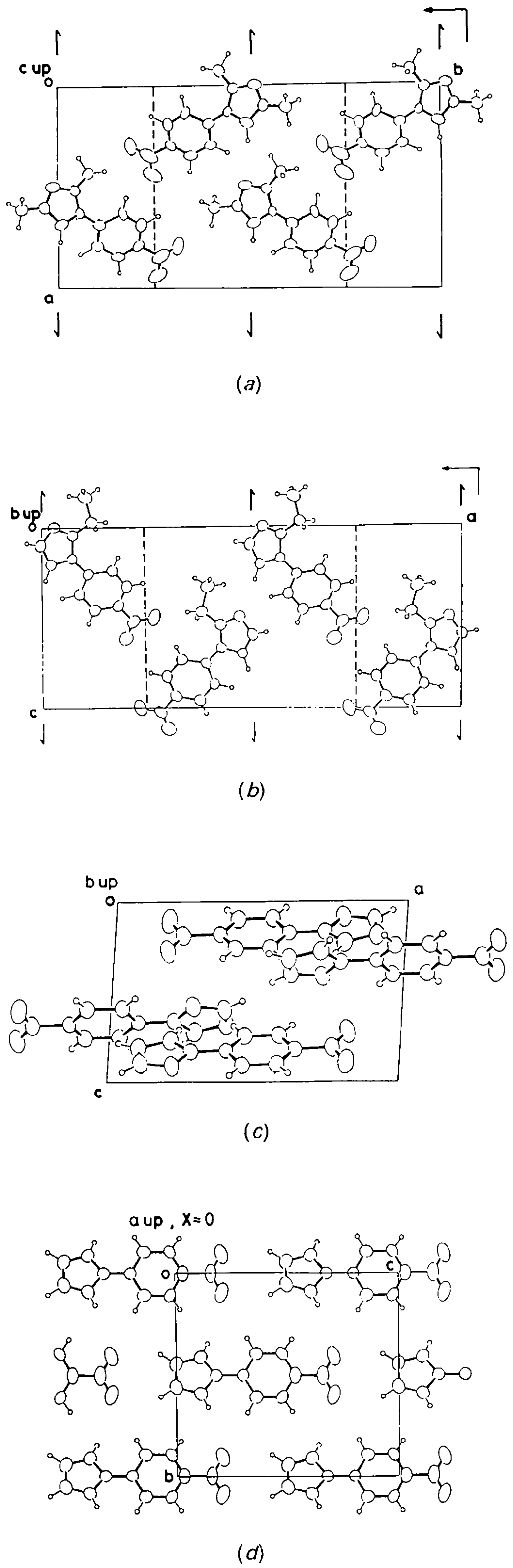
* Lists of structure factors, anisotropic thermal parameters, bond distances and angles and positional parameters of H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54143 (98 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors* (*Hamilton*, 1959)

	x	y	z	$B/B_{eq}(\text{Å}^2) \times 10$
Compound (I)				
O(11)	1329 (1)	2348 (3)	4940 (1)	63
O(12)	140 (1)	1721 (3)	3751 (1)	61
N(11)	546 (1)	2159 (3)	4544 (2)	43
N(12)	−1313 (1)	3584 (3)	6435 (1)	34
N(13)	−2170 (1)	3350 (3)	7056 (1)	41
C(11)	65 (2)	2504 (3)	5046 (2)	33
C(12)	499 (2)	3130 (4)	5914 (2)	39
C(13)	41 (2)	3464 (4)	6371 (2)	38
C(14)	−840 (2)	3181 (3)	5961 (2)	31
C(15)	−1269 (2)	2553 (4)	5082 (2)	39
C(16)	−816 (2)	2214 (4)	4617 (2)	39
C(17)	−1321 (2)	5244 (4)	6805 (2)	40
C(18)	−1848 (2)	5072 (4)	7169 (2)	40
C(19)	−1840 (2)	2479 (4)	6616 (2)	36
C(110)	−1981 (2)	533 (4)	6354 (2)	50
O(21)	4967 (1)	2597 (3)	−1410 (1)	65
O(22)	6096 (1)	3292 (3)	−191 (1)	65
N(21)	5343 (1)	2821 (3)	−601 (2)	42
N(22)	3563 (1)	1377 (3)	1367 (1)	32
N(23)	2844 (1)	1649 (3)	2143 (1)	39
C(21)	4871 (2)	2498 (3)	−86 (2)	33
C(22)	4022 (2)	1989 (4)	−540 (2)	43
C(23)	3586 (2)	1638 (4)	−55 (2)	41
C(24)	4013 (2)	1806 (3)	867 (2)	31
C(25)	4861 (2)	2369 (4)	1311 (2)	43
C(26)	5305 (2)	2700 (4)	834 (2)	43
C(27)	3371 (2)	−352 (4)	1529 (2)	41
C(28)	2938 (2)	−158 (4)	2001 (2)	39
C(29)	3227 (2)	2527 (4)	1755 (2)	35
C(210)	3287 (2)	4522 (4)	1719 (2)	62
Compound (II)				
O(1)	4422 (8)	2449 (4)	−3525 (23)	90
O(2)	2970 (8)	1893 (3)	−2369 (26)	89
N(1)	3466 (8)	2357 (4)	−2396 (23)	67
N(2)	1312 (5)	4431 (3)	2911 (18)	30
N(3)	0*	5133 (3)	3818 (20)	40
C(1)	2941 (8)	2930 (4)	−792 (28)	42
C(2)	1903 (8)	2858 (4)	606 (29)	45
C(3)	1360 (8)	3325 (3)	2037 (26)	41
C(4)	1881 (8)	3930 (4)	1643 (24)	37
C(5)	2938 (7)	3979 (4)	283 (27)	42
C(6)	3479 (7)	3450 (4)	−1055 (28)	44
C(7)	1843 (8)	4922 (4)	4371 (25)	40
C(8)	1032 (8)	5348 (3)	4869 (25)	35
C(9)	190 (8)	4572 (4)	2503 (26)	39
C(10)	1115 (8)	5941 (4)	6550 (27)	44
C(11)	−669 (9)	4216 (4)	943 (28)	42
Compound (III)				
O(1)	6990 (1)	8949 (7)	6212 (3)	70
O(2)	7673 (1)	7739 (8)	5033 (3)	73
N(1)	7182 (1)	7684 (8)	5272 (3)	47
N(2)	5713 (1)	2034 (6)	1766 (2)	31
N(3)	5290 (1)	635 (7)	0*	39
C(1)	6806 (1)	6072 (8)	4376 (3)	35
C(2)	6243 (1)	6180 (8)	4611 (3)	37
C(3)	5887 (1)	4848 (8)	3728 (3)	34
C(4)	6092 (1)	3374 (7)	2651 (3)	30
C(5)	6663 (1)	3204 (8)	2455 (3)	36
C(6)	7021 (1)	4596 (8)	3319 (3)	40
C(7)	5216 (1)	526 (8)	2096 (3)	35
C(8)	4972 (1)	−301 (8)	1020 (3)	40
C(9)	5734 (1)	2033 (7)	465 (3)	33
C(10)	6192 (1)	3537 (8)	−282 (3)	38
C(11)	6043 (1)	3892 (10)	−1661 (3)	53
Compound (IV)				
O(1*A*)	−3580 (3)	10518 (3)	1558 (3)	91
O(2*A*)	−1763 (4)	11911 (2)	1717 (3)	104
N(1*A*)	−2266 (4)	10997 (3)	1876 (3)	63
N(2*A*)	1861 (3)	8794 (2)	4277 (2)	38
N(3*A*)	2917 (3)	7486 (3)	5041 (2)	50
C(1*A*)	−1182 (4)	10385 (3)	2475 (3)	46
C(2*A*)	−1727 (4)	9422 (3)	2776 (3)	46
C(3*A*)	−712 (4)	8901 (3)	3391 (3)	40
C(4*A*)	809 (4)	9332 (3)	3651 (3)	36
C(5*A*)	1332 (4)	10294 (3)	3323 (3)	48
C(6*A*)	317 (5)	10836 (3)	2738 (3)	53
C(7*A*)	3100 (4)	9421 (3)	5159 (3)	47
C(8*A*)	3697 (4)	8618 (3)	5601 (3)	54
C(9*A*)	1802 (4)	7611 (3)	4241 (3)	39
C(10*A*)	731 (4)	6624 (3)	3380 (3)	37
C(11*A*)	303 (4)	6584 (3)	2248 (3)	43
C(12*A*)	−670 (4)	5599 (3)	1470 (3)	54
C(13*A*)	−1201 (4)	4658 (3)	1826 (3)	56
C(14*A*)	−769 (4)	4699 (3)	2943 (3)	56
C(15*A*)	193 (4)	5665 (3)	3722 (3)	45
O(1*B*)	1891 (4)	540 (2)	223 (3)	82
O(2*B*)	496 (3)	1743 (3)	−279 (2)	85
N(1*B*)	1597 (4)	1528 (3)	317 (3)	57
N(2*B*)	5653 (3)	5359 (2)	3597 (2)	38
N(3*B*)	6825 (3)	7196 (3)	4524 (2)	53
C(1*B*)	2636 (4)	2523 (3)	1209 (3)	41
C(2*B*)	2200 (4)	3581 (3)	1468 (3)	44
C(3*B*)	3182 (4)	4519 (3)	2272 (3)	38
C(4*B*)	4609 (4)	4390 (3)	2780 (3)	36
C(5*B*)	5026 (4)	3300 (3)	2510 (3)	44
C(6*B*)	4022 (4)	2349 (3)	1725 (3)	45
C(7*B*)	6537 (4)	5316 (3)	4622 (3)	46
C(8*B*)	7230 (4)	6432 (3)	5165 (3)	55
C(9*B*)	5875 (4)	6523 (3)	3582 (3)	40
C(10*B*)	5243 (4)	6936 (3)	2598 (3)	38
C(11*B*)	5457 (4)	6424 (3)	1552 (3)	47
C(12*B*)	4880 (5)	6847 (4)	629 (3)	61
C(13*B*)	4130 (5)	7772 (3)	767 (3)	63
C(14*B*)	3919 (4)	8276 (3)	1793 (3)	57
C(15*B*)	4480 (4)	7876 (3)	2719 (3)	47
Compound (V)				
O(1)	−3169 (1)	2397 (1)	6063 (2)	54
O(2)	−3162 (1)	647 (1)	7739 (2)	52
N(1)	−2666 (1)	1489 (2)	6876 (2)	39
N(2)	2192 (1)	1131 (1)	6653 (2)	29
N(3)	2814 (1)	2088 (2)	5856 (3)	39
C(1)	−1398 (1)	1398 (2)	6804 (3)	30
C(2)	−805 (2)	2381 (2)	5976 (3)	33
C(3)	388 (2)	2297 (2)	5916 (3)	32
C(4)	970 (1)	1232 (2)	6710 (2)	26
C(5)	356 (2)	248 (2)	7535 (3)	33
C(6)	−836 (2)	330 (2)	7578 (3)	33
C(7)	3899 (2)	1657 (2)	6007 (3)	39
C(8)	3993 (2)	459 (2)	6869 (3)	39
C(9)	2898 (2)	140 (2)	7269 (3)	36
Compound (VI)				
Cl(1)	−1513 (1)	0*	−700 (3)	41
Cl(2)	2264 (1)	−2062 (1)	−5496 (4)	53
O(1)	−6039 (3)	−4107 (5)	−2821 (17)	96
O(2)	−5007 (4)	−5398 (4)	−382 (15)	75
N(1)	−5087 (3)	−4488 (4)	−1726 (12)	50
N(2)	−931 (3)	−1999 (3)	−3381 (8)	28
N(3)	31 (3)	−2568 (3)	−4592 (11)	32
N(4)	537 (3)	−783 (3)	−3001 (10)	36
C(1)	−4013 (4)	−3819 (4)	−2129 (12)	34
C(2)	−4120 (4)	−2751 (4)	−3537 (12)	36
C(3)	−3095 (3)	−2128 (4)	−3955 (11)	31
C(4)	−2001 (3)	−2595 (3)	−2920 (11)	28
C(5)	−1921 (3)	−3662 (3)	−1494 (11)	31
C(6)	−2948 (4)	−4274 (4)	−1079 (11)	35
C(7)	−568 (4)	−949 (4)	−2444 (11)	32
C(8)	860 (4)	−1791 (4)	−4295 (11)	35
Compound (VII)				
O(1)	210 (3)	5942 (3)	7079 (3)	77
N(1)	0	5000	6591 (4)	53
N(2)	0	5000	1791 (3)	36
C(1)	0	5000	5344 (4)	43
C(2)	220 (3)	6064 (3)	4765 (3)	44
C(3)	218 (3)	6061 (3)	3601 (3)	43
C(4)	0	5000	3006 (4)	33
C(5)	399 (3)	5889 (3)	1094 (3)	43
C(6)	259 (3)	5560 (3)	0*	47

* This parameter was used to define the unit-cell origin and is listed without e.s.d.



(*a*)

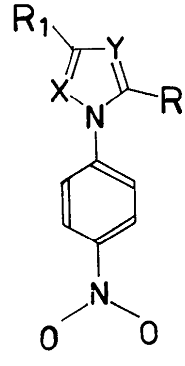
(*b*)

(*c*)

(*d*)

Fig. 1. Projection of the crystal structure of (*a*) (II) along *c*, (*b*) (III) along *b*, and (*c*) (V) along *b*. (*d*) Partial projection of the crystal structure of (VII) along *a* around $x = 0$.

(V): Colorless plate-like crystals (110) from an acetone solution, 0.30 × 0.35 × 0.55 mm. h $-14 \rightarrow 14$, k $0 \rightarrow 13$, l $0 \rightarrow 9$ ($2\theta \leq 55°$), θ–2θ scan, 2091 reflections measured, 1295 observed, 1188 unique ($0.963 < A < 0.972$, $R_{\text{int}} = 0.010$). $R = 0.045$, $wR = 0.046$, $S = 1.76$, $(\Delta/\sigma)_{\max} = 0.36$, $-0.40 < \Delta\rho < 0.20$ e Å^{-3}. (VI): Colorless plate-like crystals (100) elongated along *b* by sublimation, 0.12 × 0.30 × 0.60 mm. Peak half-width of 0.20 ~ 0.38°, ω scan, h $-14 \rightarrow 14$, k $0 \rightarrow 15$, l $-4 \rightarrow 4$ ($2\theta \leq 55°$), 2408 reflections measured, 1193 observed, 639 unique ($0.838 < A < 0.927$, $R_{\text{int}} = 0.011$). Systematic absences $0k0$, k odd suggested the space group $P2_1$ or $P2_1/m$. Since $Z = 2$ with no molecular symmetry, the space group was determined to be $P2_1$. Structural chirality determined by the anomalous scattering of Cl, final $R = 0.023$, $wR = 0.032$, $S = 1.82$, $(\Delta/\sigma)_{\max} = 0.14$, $-0.15 < \Delta\rho < 0.16$ e Å^{-3}. (VII): Pale yellow distorted-octahedal crystals from an acetone solution, 0.40 × 0.40 × 0.30 mm. h $0 \rightarrow 19$, k $0 \rightarrow 15$, l $0 \rightarrow 16$ ($2\theta \leq 60°$), θ–2θ scan, 669 reflections measured, 342 unique reflections observed (no absorption correction). *F*-centered orthorhombic unit cell with additional systematic absences $0kl$, $k + l \neq 4n$ and $h0l$ $h + l \neq 4n$. The molecule lies on a twofold axis parallel to *c*, $R = 0.044$, $wR = 0.040$, $S = 1.54$, $(\Delta/\sigma)_{\max} = 0.42$, $-0.25 < \Delta\rho < 0.15$ e Å^{-3}.



(I)	X=CH,	Y=N,	R_1=H,	R_2=CH_3
(II)	X=CH,	Y=N,	R_1=R_2=CH_3	
(III)	X=CH,	Y=N,	R_1=H,	R_2=C_2H_5
(IV)	X=CH,	Y=N,	R_1=H,	R_2=C_6H_5
(V)	X=N,	Y=CH,	R_1=R_2=H	
(VI)	X=Y=N,		R_1=R_2=Cl	
(VII)	X=Y=CH,		R_1=R_2=H	

The structure of 1-(4-nitrophenyl)imidazole could not be determined properly because the crystals are twinned with cells having a common *bc* plane. $C_9H_7N_3O_2$, prisms elongated along *c*, monoclinic *Pa*, $a = 14.620$ (3), $b = 7.956$ (2), $c = 3.698$ (1) Å, $\beta =$

95.22 (2)°, $V = 428.4$ (2) Å^3, $Z = 2$, $D_x = 1.47$ Mg m^{-3}, $R = 0.147$ for 339 unique reflections.

Related literature. Crystals studied in the present work are part of a series of compounds prepared to explore new nonlinear optical materials with high transparencies for blue light (Okazaki, Shishido & Kubodera, 1987). The internal C—C—C angle of the benzene ring to which NO$_2$ is bonded ranges from 121.1 (4) to 124.8 (9)°. For the series, the σ-electron-withdrawing character of the NO$_2$ group (Di Rienzo, Domenicano & Di Sanseverino, 1980) is suggested.

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Structure of 9-Amino-2,7-di-*tert*-butylacridine

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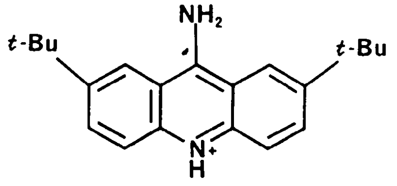
Abstract. C$_{21}$H$_{28}$N$_2^+$.Cl$^-$.H$_2$O, $M_r = 361.94$, trigonal, $P3_1$, $a = 11.086$ (2), $c = 14.367$ (4) Å, $V = 1529.2$ Å^3, $F(000) = 585$, $Z = 3$, $D_x = 1.179$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 17.34$ cm^{-1}, $T = 293$ K, final $R = 0.067$ for 3252 reflections. There is an extensive network of hydrogen-bonding interactions centered around the chloride ions positioned on the threefold axes. This is effectively a channel into which the 9-amino groups of the title compound are directed and hydrogen bond to the chloride ions. These groups and the protonated ring N atoms also form hydrogen bonds to water molecules present in the channel.

Experimental. The title compound (shown in the scheme below) was crystallized from ethanol as deep-yellow hexagonal tablets. A crystal of dimensions 0.3 × 0.3 × 0.1 mm was used in the analysis. Accurate cell dimensions were obtained by least-squares analysis of 25 reflections (8 < θ < 17°) measured on an Enraf–Nonius CAD-4 diffractometer. Intensity data were collected at room temperature with graphite-monochromated Cu $K\alpha$ radiation in the range $1.5 \leq \theta \leq 70°$ ($0 \leq h \leq 13$, $-17 \leq l \leq 17$) using an ω–2θ scan technique and a maximum scan time of 120 s per reflection. The intensities of three strong reflections were monitored at regular intervals during the data collection and showed no decay (< 3%). A unique data set of 6009 reflections was collected, 3252 had $I \geq 1.5\sigma(I)$. Lorentz, polarization and a (post refinement) absorption correction (Walker & Stuart, 1983) were applied to the data. Maximum and minimum transmission coefficients were 1.23 and 0.81. Systematic absences 00l, $l = 3n$ were found. Direct methods (*MULTAN*82; Main *et al.*, 1982) were applied to both enantiomorphic space groups $P3_1$, and $P3_2$. The best E map for the latter had a combined figure of merit (CFOM) of 1.452; the map could not be interpreted. The best E map in $P3_1$ had a CFOM of 2.911 and showed all the non-H atoms in the structure together with a chloride ion and a water molecule of crystallization, the former on the crystallographic threefold axis. Refinement was by full-matrix least squares based on F. The positions of some H atoms, including those on the water molecule, were located in difference Fourier maps. Others, especially on the butyl groups, were gener-



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