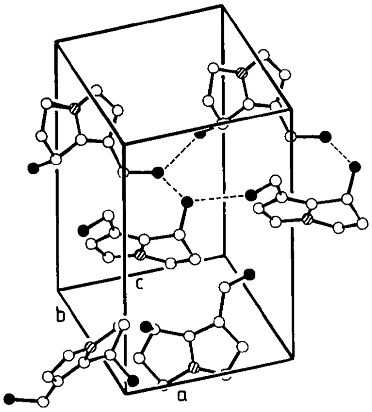

Fig. 2. The crystal packing.

The molecular packing is illustrated in Fig. 2. Two intermolecular hydrogen bonds in the crystal link the molecules into sheets parallel to the *ab* plane. The hydroxyl oxygen at C(7) acts as the donor in the interaction with the hydroxyl oxygen at C(9) of a molecule related by a cell translation along **a**; the O(11)···O(10), H(11)···O(10) and O(11)—H(11) distances are 2·739 (4), 1·93 (5) and 0·82 (7) Å, respectively, with the angle O(11)—H(11)···O(10) 169 (5)°. In the other interaction, O(10) is the donor to O(11) of a molecule related by the screw axis along **b** ($x = 0$, $z = \frac{3}{4}$); the O(10)···O(11), O(10)···H(11) and O(10)—H(10) distances have the respective values of 2·807 (4), 2·26 (5) and 0·64 (7) Å and the O(10)—H(10)···O(11) angle is 145 (5)°. All other intermolecular contacts are normal.

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References

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Culvenor, C. C. J., Edgar, J. A., Smith, L. W. & Tweeddale, H. J. (1970). *Aust. J. Chem.* **23**, 1853–1867.
Huxtable, R. J. (1979). *Gen. Pharmacol.* **10**, 159–167.
Huxtable, R. J. (1980). *Trends Pharmacol. Sci.* **1**, 299–303.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Mackay, M. F., Sadek, M., Culvenor, C. C. J. & Smith, L. W. (1983). *Acta Cryst.* C**39**, 1230–1233.
Mackay, M. F., Sadek, M., Culvenor, C. C. J. & Smith, L. W. (1984). *Acta Cryst.* C**40**, 473–476.
McLean, E. K. (1970). *Pharmacol. Rev.* **22**, 429–483.
Sheldrick, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1985). C**41**, 1106–1108

Chromotropisms of Imidazole Derivatives. II. Structure of 4,5-Bis(4-methoxyphenyl)-2-(4-nitrophenyl)imidazolium Acetate Dihydrate, $C_{23}H_{20}N_3O_4^+.C_2H_3O_2^-.2H_2O$

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Abstract. $M_r = 497·49$, monoclinic, $C2/c$, $a = 39·306$ (14), $b = 6·974$ (3), $c = 21·291$ (8) Å, $\beta = 121·83$ (3)°, $V = 4959$ (4) Å^3, $Z = 8$, $D_m = 1·33$ (2), $D_x = 1·33$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1·54178$ Å, $\mu = 8·51$ cm^{-1}, $F(000) = 2096$, room temperature, $R = 0·046$ for 1700 observed reflections. The imidazole ring is protonated and is in the same plane as the benzene ring containing the nitro group. Two imidazole rings related by the center of symmetry are linked to each other through four water molecules at the H—N site. The molecules are packed in sheets parallel to the *ac* plane. The hydration or dehydration of the crystal structure is related to the color change of the crystal.

Introduction. Crystallization of 4,5-bis(4-methoxyphenyl)-2-(4-nitrophenyl)imidazole from acetic acid–water gave orange crystals with one molecule of acetic acid and two molecules of water. The crystal changed its color from yellow to dark red on drying, heating or trituration. Below 343 K, the phenomena were rever-

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Table 1. *Final atomic coordinates of the non-*H *atoms* ($\times 10^4$) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*(Å^2)
O(1)	6167 (1)	2663 (7)	5081 (3)	5·92
O(2)	6319 (1)	2766 (7)	6214 (3)	6·16
N(3)	6078 (1)	2684 (7)	5552 (3)	4·16
C(4)	5644 (2)	2601 (8)	5286 (3)	3·31
C(5)	5372 (2)	2357 (9)	4548 (3)	3·93
C(6)	4970 (2)	2266 (9)	4311 (3)	3·83
C(7)	4851 (2)	2438 (7)	4820 (3)	2·99
C(8)	5134 (2)	2720 (8)	5561 (3)	3·58
C(9)	5540 (2)	2793 (8)	5808 (3)	3·79
C(10)	4422 (2)	2374 (7)	4566 (3)	2·86
N(11)	4113 (1)	2402 (6)	3866 (2)	2·97
C(12)	3761 (2)	2374 (7)	3868 (3)	3·07
C(13)	3864 (2)	2332 (7)	4592 (3)	2·91
N(14)	4280 (1)	2317 (6)	5018 (2)	2·88
C(15)	3628 (2)	2351 (8)	4945 (3)	2·81
C(16)	3288 (2)	3517 (8)	4670 (3)	3·52
C(17)	3079 (2)	3543 (9)	5022 (4)	3·98
C(18)	3204 (2)	2480 (9)	5653 (3)	3·72
C(19)	3540 (2)	1319 (9)	5932 (3)	3·62
C(20)	3745 (2)	1275 (9)	5570 (3)	3·21
O(21)	2978 (1)	2647 (6)	5970 (2)	5·43
C(22)	3109 (2)	1628 (10)	6643 (4)	7·62
C(23)	3370 (2)	2391 (8)	3170 (3)	2·95
C(24)	3305 (2)	3534 (8)	2589 (3)	3·28
C(25)	2942 (2)	3554 (8)	1922 (3)	3·22
C(26)	2634 (2)	2411 (9)	1841 (3)	3·23
C(27)	2690 (2)	1275 (9)	2421 (3)	3·65
C(28)	3055 (2)	1235 (8)	3077 (3)	3·42
O(29)	2264 (1)	2305 (5)	1213 (2)	4·29
C(30)	2190 (2)	3474 (12)	602 (4)	5·06
O(31)	4163 (1)	5255 (6)	2653 (2)	5·25
C(32)	4162 (2)	3690 (12)	2382 (3)	4·24
C(33)	4175 (3)	3613 (10)	1701 (4)	8·41
O(34)	4144 (1)	2094 (6)	2666 (2)	3·86
O(35)	4715 (2)	1721 (8)	6522 (2)	6·03
O(36)	4471 (1)	1379 (5)	7535 (2)	3·94

* B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

sible but above 343 K, the crystal gradually lost its solvents irreversibly (Sakaino, Fukuda, Inouye & Kakisawa, 1985). In order to clarify the relation between the color and the molecular geometry, the crystal structure of the title compound is reported here.

Experimental. Orange prisms, grown from acetic acid–water solution; D_m by flotation in aqueous KI; systematic absences (from Weissenberg photographs) hkl for $h + k = 2n$ and $h0l$ for $l = 2n$ ($h = 2n$), space group $C2/c$ or Cc; centrosymmetric choice confirmed by successful refinement; crystal $0{\cdot}43 \times 0{\cdot}43 \times 0{\cdot}08$ mm; Rigaku AFC-5 automated four-circle diffractometer; graphite-monochromated Cu $K\alpha$ radiation, 40 kV and 180 mA; unit-cell dimensions by least-squares refinement from 25 reflections with $24 < 2\theta < 33°$; 2θ–ω scan, scan rate 2° min^{-1}, $\Delta\omega = (2{\cdot}0 + 0{\cdot}5\tan\theta)°$; three standard reflections measured every 56 reflections with ±2% fluctuation; 2287 unique reflections, $2\theta = 95°$ ($0 \le h \le 37$, $0 \le k \le 6$, $-20 \le l \le 20$); 1700 reflections with $|F_o| > 3\sigma(F_o)$ used for structure determination; intensities corrected for Lorentz and polarization, not for absorption; structure solved by direct methods (*MULTAN*80, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); first E map revealed positions of 20 non-H atoms including the imidazole ring; successive difference Fourier syntheses determined positions of all non-H atoms; structure refined by full-matrix least squares with *RFINE*2 (Finger, 1969), $R = 0{\cdot}125$ for anisotropic temperature factors; all H atoms but those bonded to C(22), C(33), and O(36) located from difference Fourier synthesis; non-located H atoms given fixed geometries O—H and C—H 1·00 and 1·08 Å respectively, and assigned equivalent isotropic temperature factor of bonded non-H atom; final refinement on F with anisotropic temperature factors for all non-H atoms and with isotropic H atoms (except H atoms mentioned above), $R = 0{\cdot}046$, $wR = 0{\cdot}056$, $w = 1/\sigma^2(F_o)$; $|\Delta\rho|_{\max}$ in final difference Fourier map $= 0{\cdot}20$ e Å^{-3}; $(\Delta/\sigma)_{\max} = 0{\cdot}001$, $(\Delta/\sigma)_{\text{av}} = 0{\cdot}0001$; all numerical calculations carried out on a Facom M-380 computer in the Science Information Processing Center of the University of Tsukuba; scattering factors for C, N, O from Cromer & Mann (1968) and for H from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters are listed in Table 1.* The molecular structure of the compound is illustrated in Fig. 1, projected on the ac plane, together with the atomic-numbering scheme. The bond distances and angles are listed in Table 2. The similarity of the imidazole ring geometry to that of (4-imidazolio)-acetate hydrochloride (Jones & Pauling, 1976) shows that the imidazole nitrogen is protonated by the acetic acid proton. The imidazole ring is planar and is nearly

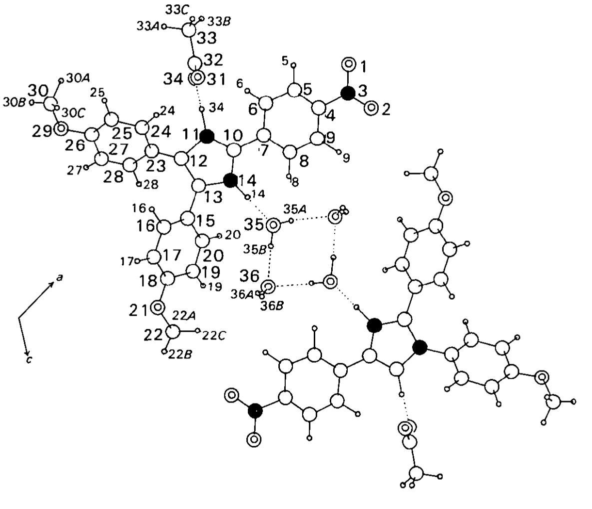

Fig. 1. Molecular structure and numbering, projected on the ac plane. ○: carbon, ●: nitrogen, ◎: oxygen. The small circles and numerals indicate the hydrogen atoms.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances involving H atoms, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42130 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in the same plane with the benzene ring containing the nitro group (dihedral angle = 9·1°). The other two benzene rings make angles of 39·9 and 139·4° with the imidazole ring. The bond distances and angles within the molecule are normal.

The crystal-packing pattern is interesting as regards its thermochromic properties. Two imidazole rings related by the center of symmetry are linked to each other through four water molecules at the H—N of the imidazole ring as shown in Fig. 1. The molecules are packed in sheets parallel to the *ac* plane, and the three-dimensional packing pattern is shown in Fig. 2 (projected on the *bc* plane), in which the imidazole plane is abbreviated as a double line. The hydrogen-bonding network, indicated as a dotted line in Figs. 1 and 2, plays an essential role in the crystal packing and the atoms participating in hydrogen-bond formation are summarized in Table 3 together with some relevant geometrical values. Reversible thermochromism agrees with the removal from, or addition into, the crystal packing of one water molecule, O(35), for such a change may retain the original crystal structure. On the other hand, if the second water molecule, O(36), is removed, the three-dimensional crystal packing is destroyed and the phenomena are no longer reversible.

Almost all of the interatomic contacts between non-hydrogen atoms correspond to van der Waals distances; exceptionally two shorter cases are C(9)(*x*, *y*, *z*)···O(31)(1 − *x*, 1 − *y*, 1 − *z*) [3·152 (8) Å] and O(1)-(*x*, *y*, *z*)···C(20)(1 − *x*, 1 − *y*, 1 − *z*) [3·181 (8) Å]. With hydrogen atoms, O(31)(*x*, *y*, *z*)···H(9)(1 − *x*, 1 − *y*, 1 − *z*) [2·25 (6) Å] and O(21)(*x*, *y*, *z*)···H(25)-(1 + *x*, 1 − *y*, $\frac{1}{2}$ + *z*) [2·46 (5) Å] have significant *d* values, 0·45 and 0·24 respectively (Taylor & Kennard, 1982).

Table 2. *Bond distances* (Å) *and angles* (°) *with their standard deviations in parentheses*

O(1)–N(3)	1·224 (10)	C(15)–C(20)	1·376 (8)
O(2)–N(3)	1·216 (7)	C(16)–C(17)	1·373 (13)
N(3)–C(4)	1·488 (8)	C(17)–C(18)	1·375 (10)
C(4)–C(5)	1·368 (7)	C(18)–C(19)	1·388 (9)
C(4)–C(9)	1·378 (11)	C(19)–C(20)	1·378 (12)
C(5)–C(6)	1·382 (9)	C(18)–O(21)	1·375 (11)
C(6)–C(7)	1·395 (11)	O(21)–C(22)	1·429 (10)
C(7)–C(8)	1·384 (7)	C(23)–C(24)	1·374 (9)
C(8)–C(9)	1·393 (9)	C(23)–C(28)	1·400 (9)
C(7)–C(10)	1·473 (8)	C(24)–C(25)	1·384 (7)
C(10)–N(11)	1·336 (6)	C(25)–C(26)	1·381 (9)
C(10)–N(14)	1·346 (10)	C(26)–C(27)	1·382 (10)
N(11)–C(12)	1·386 (9)	C(27)–C(28)	1·377 (7)
C(12)–C(13)	1·374 (9)	C(26)–O(29)	1·363 (5)
C(13)–N(14)	1·390 (7)	O(29)–C(30)	1·426 (10)
C(12)–C(23)	1·471 (6)	O(31)–C(32)	1·235 (9)
C(13)–C(15)	1·468 (10)	C(32)–C(33)	1·479 (12)
C(15)–C(16)	1·404 (8)	C(32)–O(34)	1·285 (9)

O(1)–N(3)–O(2)	124·5 (6)	C(13)–C(15)–C(20)	120·6 (5)
O(1)–N(3)–C(4)	117·1 (5)	C(16)–C(15)–C(20)	118·5 (7)
O(2)–N(3)–C(4)	118·5 (7)	C(15)–C(16)–C(17)	119·6 (6)
N(3)–C(4)–C(5)	119·1 (7)	C(16)–C(17)–C(18)	121·0 (6)
N(3)–C(4)–C(9)	117·3 (5)	C(17)–C(18)–C(19)	120·1 (8)
C(5)–C(4)–C(9)	123·7 (6)	C(17)–C(18)–O(21)	116·2 (6)
C(4)–C(5)–C(6)	118·4 (7)	C(19)–C(18)–O(21)	123·7 (6)
C(5)–C(6)–C(7)	120·1 (5)	C(18)–C(19)–C(20)	118·7 (6)
C(6)–C(7)–C(8)	120·0 (6)	C(15)–C(20)–C(19)	122·1 (6)
C(6)–C(7)–C(10)	120·1 (4)	C(18)–O(21)–C(22)	117·7 (6)
C(8)–C(7)–C(10)	120·0 (7)	C(12)–C(23)–C(24)	120·8 (6)
C(7)–C(8)–C(9)	120·6 (7)	C(12)–C(23)–C(28)	120·9 (5)
C(8)–C(9)–C(4)	117·4 (5)	C(23)–C(24)–C(25)	122·0 (6)
C(7)–C(10)–N(11)	126·9 (6)	C(24)–C(25)–C(26)	118·9 (6)
C(7)–C(10)–N(14)	124·4 (4)	C(25)–C(26)–C(27)	120·1 (5)
N(11)–C(10)–N(14)	108·7 (5)	C(25)–C(26)–O(29)	124·5 (6)
C(10)–N(11)–C(12)	108·6 (5)	C(27)–C(26)–O(29)	115·5 (6)
N(11)–C(12)–C(13)	107·6 (4)	C(26)–C(27)–C(28)	120·5 (7)
N(11)–C(12)–C(32)	120·7 (6)	C(23)–C(28)–C(27)	120·1 (6)
C(12)–C(13)–N(14)	106·2 (6)	C(24)–C(23)–C(28)	118·3 (4)
C(12)–C(13)–C(15)	133·2 (4)	C(26)–O(29)–C(30)	117·5 (5)
C(13)–C(12)–C(23)	131·7 (6)	O(31)–C(32)–C(33)	120·0 (7)
C(15)–C(13)–N(14)	120·6 (5)	O(31)–C(32)–O(34)	122·2 (7)
C(13)–N(14)–C(10)	108·9 (4)	C(33)–C(32)–O(34)	117·8 (7)
C(13)–C(15)–C(16)	120·9 (5)		

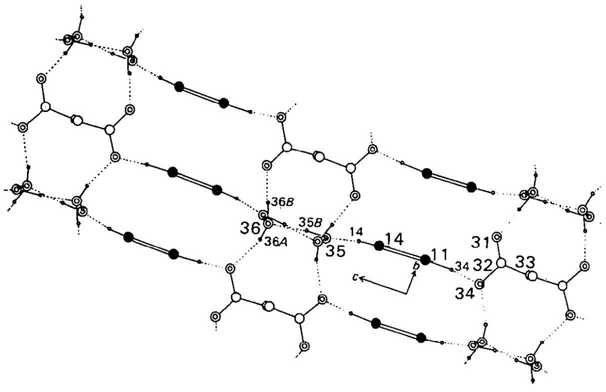

Fig. 2. Three-dimensional crystal packing projected on the *bc* plane. Double lines show the imidazole ring.

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°) *of the type X*—H···*Y*

E.s.d.'s in angles are 2–4°.

X	*Y*	*X*···*Y*	*X*—H	H···*Y*	*X*—H···*Y*
N(11)—H(34)	O(34)	2·630 (7)	1·20 (7)	1·44 (7)	176
N(14)—H(14)	O(35)	2·751 (6)	1·08 (5)	1·67 (5)	173
O(35)—H(35*B*)	O(36)	2·794 (8)	1·02 (8)	1·77 (8)	175
O(35)—H(35*A*)	O(36ⁱ)	2·748 (6)	0·82 (9)	1·93 (8)	175
O(36)—H(36*B*)	O(31ⁱⁱ)	2·716 (6)	1·0*	1·7*	172*
O(36)—H(36*A*)	O(34ⁱⁱⁱ)	2·820 (6)	1·0*	1·9*	158*

Symmetry code: (i) 1 − *x*, *y*, $\frac{3}{2}$ − *z*; (ii) *x*, 1 − *y*, $\frac{1}{2}$ + *z*; (iii) *x*, −*y*, $\frac{1}{2}$ + *z*.

* H-atom positions were not refined.

References

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Finger, L. W. (1969). *RFINE2. A System of Fortran* IV *Computer Programs for Crystal Structure Computations.* Geophysical Laboratory, Carnegie Institution, Washington, DC.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 99. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Jones, G. P. & Pauling, P. J. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 34–36.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Sakaino, Y., Fukuda, J., Inouye, Y. & Kakisawa, H. (1985). In preparation.

Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.