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2,4-Diaminoazobenzene Hydrochloride Dihydrate (Chrysoidine S.L.)

By D. Moreiras* and J. Solans

Departamento de Cristalografía y Mineralogía, Universidad de Oviedo, Arias de Velasco s/n, Oviedo, Spain

X. Solans and C. Miravitlles

Departamento de Cristalografía y Mineralogía, Universidad de Barcelona, UEI de Rayos-X y Estructuras Cristalinas, Instituto 'Jaime Almera', CSIC, Gran Vía 585, Barcelona-7, Spain

and G. Germain and J. P. Declercq

Laboratoire de Chimie-Physique et de Cristallographie, Université de Louvain, 1 place Louis Pasteur, B-1348 Louvain-la-Neuve, Belgium

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Abstract. $C_{12}H_{13}N_4^+.Cl^-.2H_2O$, triclinic, $P\bar{1}$, a = 15·097 (9), b = 10·396 (6), c = 10·234 (5) Å, α = 113·91 (5), β = 100·01 (5), γ = 80·73 (5)°, V = 1438·7 Å^3, $Z = 4$, $D_m = 1·34$, $D_c = 1·314$ Mg m^{-3}. The structure was solved with *MULTAN*. The final R value is 0·051 for all observed reflections. The protonated 2,4-diaminoazobenzene cation is nearly planar. The electronic structure of the ion is explained from the geometrical results.

Introduction. A systematic structure resolution of acid–base indicators is currently being carried out in our Departments. The title compound is the second of the series. The first was 4-dimethylaminoazobenzene-2′-carboxylic acid (methyl red) (Moreiras, Solans, Solans, Miravitlles, Germain & Declercq, 1980).

Yellow prismatic crystals of the title compound were obtained by crystallization of a commercial product from ethanol solution. A crystal 0·2 × 0·2 × 0·3 mm was used for crystal data and intensity measurements on a Syntex four-circle diffractometer. The unit cell was measured by automatically centring 15 independent reflections and refining the orientation matrix and unit-cell parameters by least squares. Intensities were collected with Mo $K\alpha$ radiation using the ω-scan technique, with a scan interval of −0·8° to +0·8°. 4521 independent reflections were measured within the range $1 \leq \theta \leq 23·5°$. 3208 of these were treated as observed, having $I \geq 2·5\sigma(I)$. Lorentz–polarization corrections were applied.

The structure was solved with the *MULTAN* system of computer programs (Main, Woolfson, Lessinger, Germain & Declercq, 1977). 334 reflections and 2500 $\sum_2$ relationships were used in the phase-determining procedure. An E map computed with the phases from the set with the highest figure of merit revealed peaks for all non-hydrogen atoms.

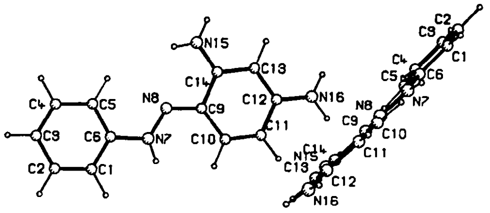

Fig. 1. View of molecules *A* and *B* drawn by *PLUTO*, showing the numbering of the atoms.

The structure was refined isotropically and anisotropically with *SHELX* (Sheldrick, 1976). A difference synthesis revealed the peaks for all non-water H atoms. The refinement was terminated at $R = 0·051$ for all observed reflections, where R is defined as $\sum||F_o| - |F_c||/\sum|F_o|$.†

The final atomic parameters are listed in Table 1. Fig. 1 showing a view of the molecules with the numbering of the atoms was drawn by *PLUTO*78 (Motherwell & Clegg, 1978).

Discussion. The bond distances and angles are shown in Fig. 2. The azobenzene skeleton is nearly planar

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* This paper reports part of the research work undertaken to satisfy the requirements for a DSc degree.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35769 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters* ($\times 10^4$, *for* H *atoms* $\times 10^3$) *and isotropic thermal parameters*

$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$. For H atoms $U = 0{\cdot}069$ (3) Å^2.

	Molecule *A*				Molecule *B*			
	x	*y*	*z*	U_{eq} (Å^2)	*x*	*y*	*z*	U_{eq} (Å^2)
C(1)	6885 (3)	8956 (5)	−347 (5)	0·06	−581 (3)	8971 (4)	5934 (4)	0·05
C(2)	7409 (3)	9441 (5)	−1006 (5)	0·07	−369 (3)	9447 (5)	7405 (4)	0·06
C(3)	7381 (3)	10885 (5)	−666 (5)	0·07	503 (3)	9256 (5)	8010 (5)	0·04
C(4)	6845 (3)	11820 (5)	332 (5)	0·07	1180 (3)	8599 (6)	7116 (5)	0·05
C(5)	6314 (3)	11366 (5)	1009 (5)	0·06	972 (3)	8104 (5)	5642 (4)	0·06
C(6)	6341 (2)	9924 (4)	660 (4)	0·05	89 (3)	8310 (4)	5042 (4)	0·04
N(7)	5792 (2)	9386 (4)	1268 (4)	0·05	−138 (2)	7862 (3)	3544 (3)	0·04
N(8)	5251 (2)	10279 (3)	2185 (3)	0·04	505 (2)	7296 (3)	2702 (3)	0·04
C(9)	4733 (3)	9835 (4)	2784 (4)	0·04	333 (2)	6925 (3)	1293 (4)	0·04
C(10)	4643 (3)	8394 (4)	2567 (5)	0·05	−533 (3)	7066 (4)	478 (4)	0·05
C(11)	4107 (3)	8106 (4)	3305 (5)	0·06	−608 (3)	6652 (4)	−960 (4)	0·04
C(12)	3602 (3)	9234 (5)	4357 (4)	0·05	182 (3)	6065 (4)	−1716 (4)	0·04
C(13)	3662 (3)	10647 (5)	4598 (4)	0·06	1030 (3)	5913 (4)	−954 (4)	0·04
C(14)	4206 (3)	10966 (4)	3823 (4)	0·05	1125 (2)	6308 (4)	518 (4)	0·04
N(15)	4253 (3)	12301 (4)	4044 (5)	0·08	1926 (2)	6148 (4)	1268 (4)	0·05
N(16)	3082 (3)	8908 (5)	5079 (4)	0·07	74 (3)	5662 (4)	−3141 (4)	0·06
Cl(17)	6424 (1)	6005 (1)	460 (1)	0·06	8114 (1)	5902 (1)	4869 (1)	0·07
O(1)	7894 (2)	7787 (3)	2958 (3)	0·06	5500 (2)	15687 (3)	7267 (4)	0·08
O(2)	3822 (2)	14744 (4)	6939 (4)	0·08	7056 (2)	14135 (4)	5912 (4)	0·09
H(1)	690 (3)	784 (5)	−62 (5)		−127 (3)	913 (4)	547 (4)	
H(2)	784 (3)	870 (5)	−178 (5)		−89 (3)	996 (5)	810 (4)	
H(3)	778 (3)	1126 (5)	−119 (5)		67 (3)	961 (5)	916 (5)	
H(4)	683 (3)	1294 (5)	60 (5)		187 (3)	846 (6)	758 (5)	
H(5)	589 (3)	1211 (5)	180 (5)		150 (3)	756 (5)	496 (4)	
H(7)	593 (3)	845 (5)	102 (5)		−78 (3)	794 (5)	314 (5)	
H(10)	501 (3)	753 (4)	178 (5)		−113 (3)	749 (4)	103 (4)	
H(11)	405 (3)	702 (4)	313 (5)		−126 (3)	677 (4)	−155 (4)	
H(13)	329 (3)	1149 (5)	539 (4)		162 (3)	548 (4)	−152 (4)	
H(15′)	402 (3)	1301 (5)	484 (5)		199 (3)	641 (5)	237 (6)	
H(15″)	455 (3)	1243 (5)	347 (5)		242 (3)	562 (5)	78 (5)	
H(16′)	284 (3)	959 (5)	586 (5)		−53 (3)	569 (5)	−363 (5)	
H(16″)	307 (3)	790 (5)	493 (5)		57 (3)	542 (5)	−359 (5)	

[longest atom-to-mean-plane distance: molecule *A* = −0·120 (5) Å for C(1); molecule *B* = 0·089 (5) Å for C(3)]. The benzene ring and the diaminobenzene group are planar with largest deviations from the least-squares mean plane of 0·033 (5) Å. The dihedral angle between the two mean planes is 1·4° for molecule *A* and 5·2° for molecule *B*.

The N(7)—N(8) bond distance (1·313 Å) in the two molecules is longer than in other azobenzene structures (average value 1·23 Å) (Brown, 1966*a*,*b*; Kakati & Chaudhuri, 1968; Hope & Victor, 1969; Gilardi & Karle, 1972; Hanson, 1973; Graeber & Morosin, 1974; Kuvosaki, Kashino & Haisa, 1976; Vani & Vijayan, 1977; Moreiras, Solans, Solans, Miravitlles, Germain & Declercq, 1980), while it is shorter than the N—N single-bond distance (1·44 Å) (*International Tables for X-ray Crystallography*, 1968).

The C(6)—N(7) distances (1·41 Å) are analogous to those obtained in the previously mentioned azobenzene compounds, while the C(9)—N(8) distances (1·32 Å) are longer than the C—N double-bond distance (1·25 Å) and C(14)—N(15) and C(12)—N(16) (1·33 Å) are shorter than the C_{ar}—N distance (1·43 Å) (*International Tables for X-ray Crystallography*, 1968). The C_{ar}—C_{ar} distances in the benzene ring of the 2,4-diaminobenzene group (Fig. 2) differ from the typical values for an aromatic ring (1·395 Å).

Table 2. *Shorter intermolecular distances* (Å)

A—$B \cdots C$	d_{AC}	d_{BC}
N(7*A*)—H(7*A*)···Cl(17*A*)^{i}	3·284 (4)	2·39 (6)
N(15*B*)—H(15″)···Cl(17*A*)^{ii}	3·297 (4)	2·36 (5)
N(16*B*)—H(16′)···Cl(17*B*)^{iii}	3·327 (5)	2·37 (5)
N(16*B*)—H(16″)···Cl(17*B*)^{ii}	3·339 (5)	2·47 (5)
N(7*B*)—H(7*B*)···O(1*A*)^{iv}	2·934 (4)	2·00 (5)
N(15*A*)—H(15′)···O(2*A*)^{i}	3·113 (6)	2·21 (5)
O(1*A*)—H···Cl(17*A*)^{i}	3·226 (3)	
O(1*B*)—H···Cl(17*A*)^{v}	3·228 (4)	
O(1*A*)—H···Cl(17*B*)^{i}	3·226 (3)	
O(2*B*)—H···Cl(17*B*)^{vi}	3·197 (4)	
O(2*A*)—H···O(1*B*)^{i}	2·780 (5)	
O(1*B*)—H···O(2*B*)^{i}	2·853 (5)	

Symmetry code

(i) x,y,z
(ii) $1-x, 1-y, -z$
(iii) $x-1, y, z-1$
(iv) $x-1, y, z$
(v) $x, y+1, z+1$
(vi) $x, y+1, z$

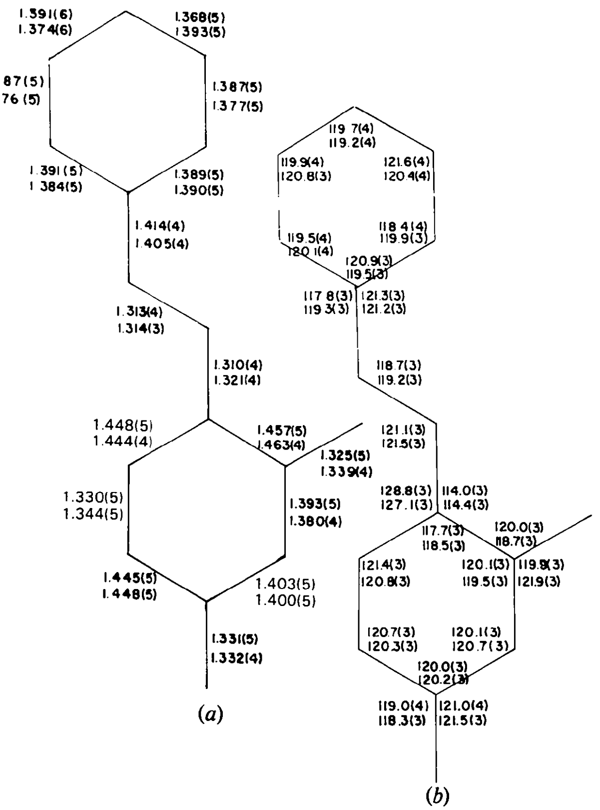

Fig. 2. (*a*) Bond distances (Å) and (*b*) bond angles (°) with standard deviations for molecules *A* (upper values) and *B* (lower).

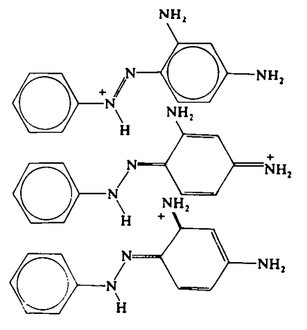

Fig. 3. Canonical forms of the protonated 2,4-diaminoazobenzene cation.

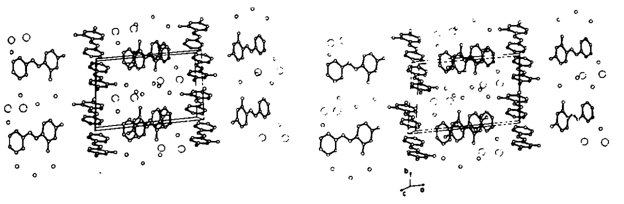

Fig. 4. Stereoview of the unit-cell contents.

All these bond-length variations are consistent with an electronic resonance for the protonated 2,4-diaminoazobenzene cation with the canonical forms shown in Fig. 3.

Shorter intermolecular contacts are given in Table 2, and a stereoview of the unit-cell contents is in Fig. 4.

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