

Fig. 3. The unit-cell contents, showing the hydrogen bridges between *A* and *B* and between *C* and *D*.

Discussion. In the tables the four molecules are referred to as *A*, *B*, *C* and *D*. Final positional parameters for the non-H atoms are listed in Table 1,* bond lengths and bond angles in Table 2. A *PLUTO*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53024 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Motherwell & Clegg, 1978) drawing of molecule *A* is given in Fig. 1.

Matching of the molecules shows that the conformations of the tricyclic systems of all four molecules are very similar [r.m.s.d. = 0.04 Å for atoms C1 up to C13 for any pair of molecules (Fig. 2)], but that for molecule *D* the relative position of the ligands of the Si atom differs from that of the other three. The dihedral angles between the planes N12, C1, Si18 and O17, C1, Si18 are 19, 20, 26 and 0° in *A–D* respectively. Both molecules *A* and *B* and molecules *C* and *D* are linked by hydrogen bridges between N12 and O16 and between O15 and O16 as is shown in Table 2 and in Fig. 3.

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Structure of 4-{2-[1-Methyl-4(1*H*)-pyridylidene]ethylidene}cyclohexa-2,5-dien-1-one Trihydrate

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Abstract. C₁₄H₁₃NO.3H₂O, *M_r* = 265.31, monoclinic, *P*2₁/*c*, *a* = 17.305 (1), *b* = 7.3128 (9), *c* = 11.7955 (9) Å, β = 110.294 (7)°, *V* = 1400.0 (3) Å³, *Z* = 4, *D_x* = 1.26 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ

= 7.23 cm⁻¹, *F*(000) = 568, room temperature, final *R* = 0.048 for 1655 observed reflections. The molecule is essentially planar, the maximum deviation of an atom from the least-squares plane through the

Table 1. Positional parameters and equivalent isotropic thermal parameters (\AA^2) of the non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = (1/6\pi^2) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
O(1)	0.7989 (1)	0.2191 (3)	0.8968 (2)	0.056 (1)
N	0.1746 (1)	0.0818 (3)	0.2985 (2)	0.049 (1)
C(1)	0.7207 (2)	0.2062 (4)	0.8330 (2)	0.045 (1)
C(2)	0.6652 (2)	0.1086 (4)	0.8746 (2)	0.052 (2)
C(3)	0.5833 (2)	0.0915 (4)	0.8037 (2)	0.052 (2)
C(4)	0.5505 (2)	0.1692 (4)	0.6876 (2)	0.046 (1)
C(5)	0.6054 (2)	0.2693 (4)	0.6476 (2)	0.050 (1)
C(6)	0.6869 (2)	0.2879 (4)	0.7169 (2)	0.051 (2)
C(7)	0.4654 (2)	0.1375 (4)	0.6162 (2)	0.050 (1)
C(8)	0.4238 (2)	0.1953 (4)	0.5031 (2)	0.051 (2)
C(9)	0.3382 (2)	0.1584 (4)	0.4364 (2)	0.047 (1)
C(10)	0.2865 (2)	0.0590 (4)	0.4831 (3)	0.054 (2)
C(11)	0.2070 (2)	0.0231 (4)	0.4142 (3)	0.054 (2)
C(12)	0.2219 (2)	0.1788 (4)	0.2505 (2)	0.054 (2)
C(13)	0.3021 (2)	0.2165 (4)	0.3157 (2)	0.053 (2)
C(14)	0.0879 (2)	0.0398 (5)	0.2259 (3)	0.067 (2)
O(2)	0.0533 (1)	0.2009 (3)	0.4740 (2)	0.075 (1)
O(3)	0.1319 (2)	0.5034 (4)	0.4042 (2)	0.087 (2)
O(4)	0.1010 (1)	0.5588 (3)	0.1609 (2)	0.065 (1)

Table 2. Bond distances (\AA) and angles ($^\circ$) of the non-H atoms with e.s.d.'s in parentheses

O(1)—C(1)	1.304 (3)	C(4)—C(7)	1.439 (3)
N—C(11)	1.353 (3)	C(5)—C(6)	1.370 (3)
N—C(12)	1.347 (4)	C(7)—C(8)	1.346 (4)
N—C(14)	1.479 (3)	C(8)—C(9)	1.441 (4)
C(1)—C(2)	1.414 (4)	C(9)—C(10)	1.405 (4)
C(1)—C(6)	1.421 (4)	C(9)—C(13)	1.407 (4)
C(2)—C(3)	1.379 (4)	C(10)—C(11)	1.359 (4)
C(3)—C(4)	1.408 (4)	C(12)—C(13)	1.361 (4)
C(4)—C(5)	1.404 (4)		
C(11)—N—C(12)	119.4 (2)	C(4)—C(5)—C(6)	121.9 (2)
C(11)—N—C(14)	120.0 (3)	C(1)—C(6)—C(5)	121.9 (3)
C(12)—N—C(14)	120.5 (2)	C(4)—C(7)—C(8)	128.1 (3)
C(2)—C(1)—O(1)	122.0 (2)	C(7)—C(8)—C(9)	125.3 (3)
C(6)—C(1)—O(1)	121.6 (3)	C(8)—C(9)—C(10)	123.8 (2)
C(2)—C(1)—C(6)	116.4 (2)	C(8)—C(9)—C(13)	120.5 (3)
C(1)—C(2)—C(3)	120.9 (2)	C(10)—C(9)—C(13)	115.7 (2)
C(2)—C(3)—C(4)	122.4 (3)	C(9)—C(10)—C(11)	121.0 (3)
C(3)—C(4)—C(5)	116.5 (2)	C(10)—C(11)—N	121.4 (3)
C(3)—C(4)—C(7)	119.3 (3)	C(13)—C(12)—N	121.2 (2)
C(5)—C(4)—C(7)	124.2 (2)	C(9)—C(13)—C(12)	121.2 (3)

two six-membered rings and the interconnecting ethyl group being 0.085 (4) \AA . The results are compared with solid-state ^{13}C -NMR spectra.

Introduction. 4-{2-[1-Methyl-4(1*H*)-pyridylidene]ethylidene}cyclohexa-2,5-dien-1-one (MPED) is a merocyanine dye that exhibits pronounced colour changes with changes of solvent polarity. The crystal structure analysis was undertaken to examine the planarity and the zwitterionic character of the molecule.

Experimental. The compound was prepared by the procedure proposed by Minch & Sadiq Shah (1977). This yielded dark claret-coloured layered crystals. The intensities were collected with an Enraf-Nonius

CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation and ω - 2θ scans. Approximate crystal dimensions 0.30 \times 0.30 \times 0.08 mm. Preliminary Weissenberg photographs indicated the crystal to be monoclinic. A total of 2640 unique reflections within the ranges $2.5 \leq \theta \leq 70^\circ$, $-21 \leq h \leq 21$, $0 \leq k \leq 8$, $0 \leq l \leq 14$ were measured, of which 1655 were above the significance level of $2.5 \sigma(I)$. Two standard reflections (320 and 011) were measured hourly, showing no significant variation during the 28 h collecting time. Unit-cell parameters by a least-squares algorithm using 23 reflections with $72 < 2\theta < 90^\circ$. Absent reflections $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$ indicated $P2_1/c$ as the space group. Corrections applied for Lorentz and polarization effects, but not for absorption. Structure determined by direct methods using the program SIMPEL83 (Schenk & Kiers, 1985). The H-atom positions were partially located in a difference Fourier map and partially calculated on the basis of standard geometry. Block-diagonal least-squares refinement on F , anisotropic for the non-H atoms and isotropic for the H atoms, converged to $R = 0.048$, $wR = 0.064$. $(\Delta/\sigma)_{\max} = 0.90$. A weighting scheme $w^{-1} = 7.30 + F_{\text{obs}} + 0.0091F_{\text{obs}}^2$ was used. The isotropic secondary extinction refined to $11(1) \times 10^{-4}$ (Zachariasen, 1968). A final difference synthesis showed residuals between -0.1 and 0.2 e \AA^{-3} . The calculations were carried out with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) unless stated otherwise. The scattering factors were taken from Cromer & Mann (1968); *International Tables for X-ray Crystallography* (1974).

The solid-state ^{13}C -NMR spectra were recorded on a Varian XL-200 NMR spectrometer using the cross-polarization magic-angle spinning method.

Discussion. Final atomic parameters for the non-H atoms are listed in Table 1.* The numbering system for the molecule is given in Fig. 1, and bond lengths and angles in Table 2.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53033 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

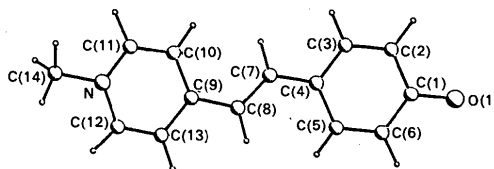


Fig. 1. The numbering of the non-H atoms.

The two six-membered rings are planar within the limits of accuracy. The molecule as a whole is approximately planar with a maximum deviation of 0.161 Å from its best plane.

The length of the central bond C(7)—C(8) of 1.346 (4) Å implies a high double-bond character [standard single- and double-bond values 1.465 (5) and 1.336 (5) Å respectively from Sutton (1965)]. This is consistent with the near planarity of the molecule. It is also in agreement with the fact that the C(1)—O(1) bond length of 1.304 (3) Å is closer to the phenolic length of 1.36 (1) Å than to the double C=O value of 1.215 (5) Å and with the planar structure around the N atom [the sum of the angles around N is 360.0 (4)°]. From this we may conclude that the molecule has the zwitterion structure (Fig. 2b).

The zwitterionic character of the structure is also corroborated by the solid-state ¹³C-NMR chemical shift data for the methyl C atoms in MPED, 1-methyl-*N*-2'-acetylphenyldihydronicotinamide and the corresponding pyridinium salt of 48, 40.4 and 50.8 p.p.m. respectively. These values indicate that the electronic structure of MPED is more closely related to that of the pyridinium compound.

Since the standard deviations for bond lengths were ≤ 0.004 Å we decided to calculate the contributions of the Kekulé structures to the molecule using the HOSE model (Krygowski, Anulewicz & Kruszewski, 1983, and references therein). Taking the entire molecule as the π -electron system we considered five canonical structures, leading to HOSE values varying from 198.1 to 230.2 kJ mol⁻¹ for one of the zwitterionic forms and for the neutral molecule respectively, indicating a contribution of 81.8% for all the zwitterion structures.

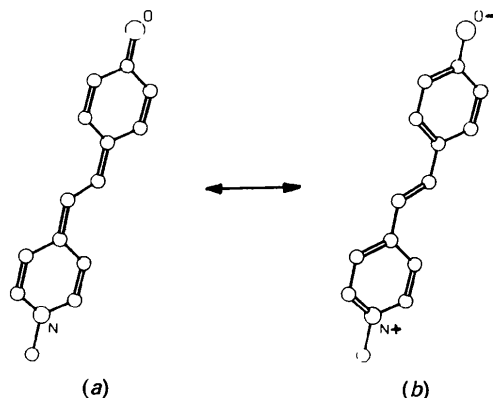


Fig. 2. Nonionic (a) and zwitterionic (b) resonance structures of MPED.

Table 3. O—O distances (Å), O—H...O angles (°) and symmetry operations of the hydrogen bonds

O(2)—H(21)...O(4)	2.792 (3)	175 (4)	$-x, -1/2 + y, 1/2 - z$
O(2)—H(22)...O(4)	2.808 (3)	171 (4)	$x, 1/2 - y, 1/2 + z$
O(3)—H(31)...O(2)	2.864 (4)	168 (4)	x, y, z
O(3)—H(32)...O(1)	2.735 (3)	179 (4)	$1 - x, 1/2 + y, 3/2 - z$
O(4)—H(41)...O(3)	2.761 (3)	169 (3)	x, y, z
O(4)—H(42)...O(1)	2.630 (3)	170 (3)	$1 - x, 1 - y, 1 - z$

In the crystal there are alternating layers, parallel to the *bc* plane, of crystal water and MPED. The water molecules are concentrated near the *bc* plane. The carbonyl end of the MPED molecule is linked to the water layer by hydrogen bonds and its methyl end is loosely surrounded by molecules of the next water layer. There are also hydrogen bonds between the water molecules. The O—O distances and the O—H...O angles of all hydrogen bonds are listed in Table 3. The MPED molecules are paired through the symmetry operation $1 - x, -y, 1 - z$, opposing the N to the O atoms. The molecules within a pair are slightly bent towards each other, the intermolecular distance at the center of the C(7)—C(8) ethyl bridge (3.49 Å) being significantly larger than the intermolecular N...O(1) distance (3.14 Å). This difference can be attributed to electrostatic and possibly to charge-transfer interactions, and is in support of our arguments for the zwitterionic structure of the molecules in the crystal.

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