Albine Perchlorate

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Abstract. $C_{14}H_{21}N_2O^+.ClO_4^-$, monoclinic, $P2_1$, $a = 8.329$ (1), $b = 11.229$ (1), $c = 8.958$ (1) Å, $\beta = 111.81$ (1)°, $Z = 2$, $D_c = 1.42$ Mg m^{-3}. The final $R = 0.066$ for 1208 reflections. Two types of hydrogen bonds were observed: $N(12)\cdots O(C4)$ of 2.772 (8) and $N(12)\cdots O(C1)$ of 2.811 (9) Å. The conformations of rings *A*, *B*, *C* are half-chair, chair and chair respectively.

Introduction. Albine (Wolińska-Mocydlarz & Wiewiórowski, 1976), previously incorrectly called 'dehydroalbine', was first investigated by X-ray methods by Tchekhlov, Kałuski, Struchkov, Wolińska-Mocydlarz & Kitaigorodskii (1974). This paper presents the results of further refinement of that structure.

Colorless crystals of albine perchlorate were obtained from ethanol solution. The dimensions of the crystal used for data collection were 0.35 × 0.40 × 0.20 mm. The measurements were carried out at room temperature on a Syntex $P2_1$ diffractometer, using Cu $K\alpha$ radiation and a graphite monochromator. The θ–2θ scan method was used with a minimum scan speed of 2° min^{-1}. Three control reflections were measured after each 55 reflections. 1354 reflections were collected including systematic absences: 1217 in the bisecting mode for $2\theta < 114°$ and 137 in the parallel mode for 2θ in the range between 116 and 130°: 1208 had $I > 1.96\sigma_I$ and were included in the subsequent calculations. Only Lorentz and polarization corrections were applied.

The crystal structure was solved by direct methods using the program *MULTAN* (Germain, Main & Woolfson, 1971). The *E* map based on the correct phase set contained 12 peaks from two rings and the allyl substituent. Positions of all remaining atoms were found on a difference Fourier map. After three cycles of isotropic full-matrix least-squares refinement with *FMLS* (Syntex, 1976), the *R* value decreased to 0.15. Three cycles of anisotropic refinement reduced the *R* value to 0.11. The positions of all H atoms were found on a difference Fourier map. They were used in the structure factor calculations, but not included in the refinement. The resultant *R* value for 1208 reflections was 0.073. The function minimized was $\sum w|F_o - F_c|^2$,

Table 1. *Fractional atomic coordinates* ($\times 10^4$ *and* $\times 10^3$ *for* H) *and isotropic thermal parameters*

	x	y	z	B_{iso} (Å^2)
Cl	6341 (2)	1344	7459 (2)	3.9 (1)
O(1)	5515 (11)	2261 (7)	6292 (7)	6.4 (4)
O(2)	7094 (15)	1920 (12)	8962 (11)	12.0 (7)
O(3)	7444 (22)	620 (11)	7114 (20)	16.7 (10)
O(4)	5044 (13)	727 (11)	7710 (17)	12.4 (8)
N(1)	1756 (6)	1042 (5)	3402 (6)	2.9 (3)
C(2)	1143 (9)	951 (7)	4582 (8)	3.5 (3)
C(3)	−197 (9)	1630 (7)	4677 (9)	3.8 (3)
C(4)	−876 (9)	2584 (7)	3583 (9)	3.4 (3)
C(5)	65 (9)	2862 (7)	2499 (9)	3.1 (3)
C(6)	715 (7)	1733 (6)	1972 (8)	2.7 (3)
C(7)	1710 (9)	1962 (6)	843 (8)	3.2 (3)
C(8)	2266 (10)	748 (7)	380 (9)	4.4 (4)
C(9)	3522 (10)	193 (7)	1909 (11)	3.8 (4)
C(10)	2603 (10)	−50 (7)	3102 (12)	3.8 (4)
C(11)	5143 (9)	958 (7)	2631 (10)	4.0 (4)
N(12)	4666 (7)	2214 (5)	2948 (7)	2.7 (2)
C(13)	3261 (9)	2786 (6)	1527 (9)	2.9 (3)
C(14)	4016 (8)	3204 (7)	322 (8)	3.5 (3)
C(15)	2703 (10)	3872 (7)	−1034 (10)	3.7 (3)
C(16)	2270 (11)	3627 (9)	−2518 (10)	9.5 (5)
O(C4)	−2116 (6)	3227 (6)	3562 (7)	1.6 (2)
H(C2)	171	35	544	7.0
H(C3)	928	154	568	7.0
H(C6)	952	121	131	7.0
H(C7)	79	242	982	7.0
H(C8)	257	89	930	7.0
H(C8)	100	33	967	7.0
H(C9)	600	433	833	7.0
H(C10)	648	472	558	7.0
H(C10)	845	429	743	7.0
H(C5)	102	337	278	7.0
H(C5)	924	323	152	7.0
H(C11)	602	77	384	7.0
H(C11)	555	112	146	7.0
H(N12)	467	233	400	7.0
H(N12)	577	269	329	7.0
H(C13)	300	367	200	7.0
H(C14)	499	374	90	7.0
H(C14)	445	269	988	7.0
H(C15)	233	467	933	7.0
H(C16)	309	302	634	7.0
H(C16)	140	412	649	7.0

where $w = \sigma_{F_o}^{-2}$. In the last three cycles of refinement the following weighting scheme was used: $w = (F_o/2.0)^2$ for $F_o < 2.0$, $w = 1$ for $2.0 \le F_o \le 13.18$ and $w =$
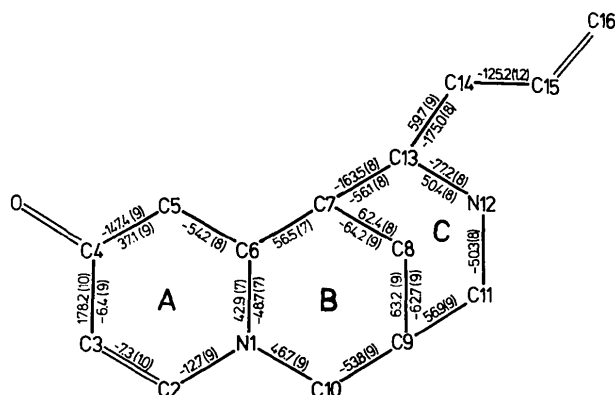
Fig. 1. Torsion angles (°) with their e.s.d.'s.
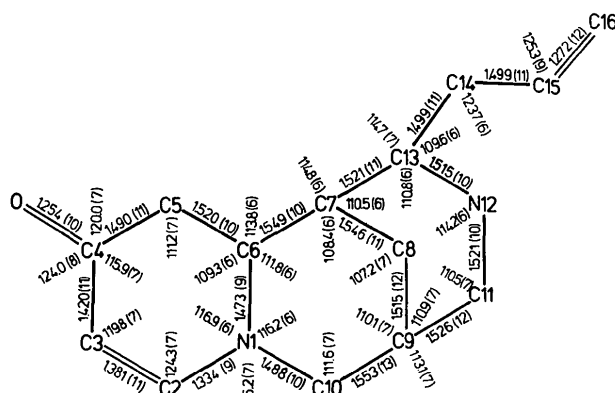
Fig. 2. Bond distances (Å) and valency angles (°) with their e.s.d.'s.

$(13 \cdot 18/F_o)^2$ for $F_o > 13 \cdot 18$. The final R and R_w values were 0·066 and 0·080 respectively. The final positional parameters are listed in Table 1.*

Discussion. A view of the albine molecule with the torsion angles is presented in Fig. 1. The three rings A, B, C have half-chair, chair and chair conformations respectively. Bond distances and angles are shown in Fig. 2. The deviations of atoms from the least-squares planes are given in Table 2.

The asymmetry parameters (Duax & Norton, 1975) for ring A are: $\Delta C_2^{2,3} = 6\cdot05$, $\Delta C_s^3 = 17\cdot44$, $\Delta C_s^1 = 43\cdot38°$; they indicate a half-chair conformation. The atoms C(2), C(3), C(4), O(C4) form a planar system with N(1) 0·164 (6) Å out of the plane. This fact and the N(1)–C(2), C(2)–C(3), C(3)–C(4) bond lengths of 1·334 (9), 1·381 (11), 1·420 (11) Å, respectively,

Table 2. *Least-squares planes*

Equations of planes

Plane (1): $-0\cdot5076X - 0\cdot6459Y - 0\cdot5702Z + 2\cdot5490 = 0$
Plane (2): $-0\cdot4336X - 0\cdot5740Y - 0\cdot6046Z + 2\cdot2378 = 0$
Plane (3): $0\cdot5203X - 0\cdot0766Y - 0\cdot8505Z + 0\cdot1704 = 0$

Deviations of atoms from the planes (Å)

Plane (1)		Plane (2)		Plane (3)	
N(1)	0·012 (6)	C(6)	0·008 (7)	C(7)	0·000 (7)
C(2)	−0·022 (8)	C(7)	−0·009 (7)	C(9)	−0·001 (9)
C(3)	0·022 (8)	C(9)	0·014 (9)	C(11)	0·000 (8)
C(4)	−0·049 (8)	C(10)	−0·014 (9)	C(13)	0·000 (7)
O(C4)	0·016 (6)	C(8)*	0·773 (8)	N(12)*	−0·594 (6)
C(5)*	−0·317 (8)	N(1)*	−0·543 (6)	C(8)*	0·754 (8)
C(6)*	0·388 (7)	χ^2	8·24	χ^2	0·01
χ^2	68·37				

* Atoms not included in plane calculations.

indicate the existence of p–n overlap between a free electron pair of the N atom and the conjugated double-bond system. These results are similar to those obtained for the structure of multiflorine perchlorate semihydrate (Pyżalska & Borowiak, 1980). For the B and C rings the asymmetry parameters are: $\Delta C_s^1 = 2\cdot06$, $\Delta C_2^{1,10} = 5\cdot92$, $\Delta C_s^{6,7} = 16\cdot01°$ and $\Delta C_s^8 = 0\cdot50$, $\Delta C_2^{8,9} = 5\cdot65$, $\Delta C_2^{7,13} = 12\cdot22°$, respectively, indicating chair conformations for both rings. These chair rings are slightly flattened in the directions of N(1) and N(12) and sharpened in the direction of C(8); this is clearly shown in Table 2. The allyl substituent is in an axial position. All bond lengths and angles are in good agreement with those reported by Tchekhlov *et al.* (1974). The unit-cell contents and molecular packing
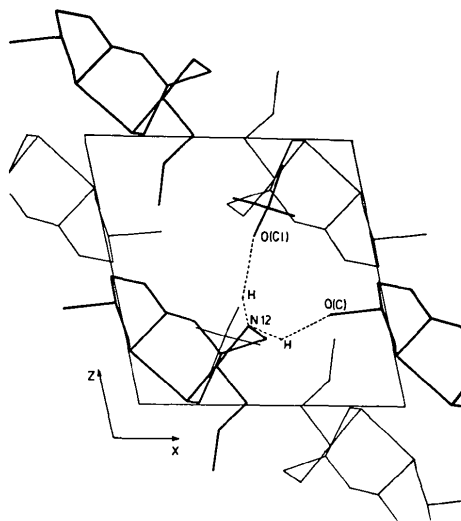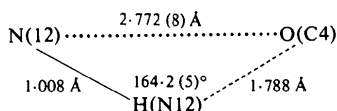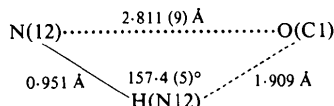

Fig. 3. Projection of the structure along [010].

are presented in Fig. 3. The molecules are linked in infinite chains by a system of hydrogen bonds:

$$N(12) \cdots\cdots \overset{2 \cdot 772\,(8)\,\text{Å}}{\cdots\cdots\cdots\cdots\cdots} O(C4)$$

$$1 \cdot 008\,\text{Å} \searrow \quad \overset{164 \cdot 2\,(5)^\circ}{} \nearrow 1 \cdot 788\,\text{Å}$$

$$H(N12)$$

where O(C4) denotes the O atom of a molecule at $x + 1$, y, z. There is another hydrogen bond between the N(12) and O(C1) atoms:

$$N(12) \cdots\cdots \overset{2 \cdot 811\,(9)\,\text{Å}}{\cdots\cdots\cdots\cdots\cdots} O(C1)$$

$$0 \cdot 951\,\text{Å} \searrow \quad \overset{157 \cdot 4\,(5)^\circ}{} \nearrow 1 \cdot 909\,\text{Å}$$

$$H(N12)$$

The existence of bifurcated hydrogen bonding was assumed between the N(12), N(1) and O(C11) atoms. The angle N(1)—H(N12)—N(12) is 93·3 (4)°. As the distance of 2·917 (9) Å between N(1) and N(12) is too large, and the free electron pair of N(1) is involved in a conjugated double-bond system, we had to discount this possibility.

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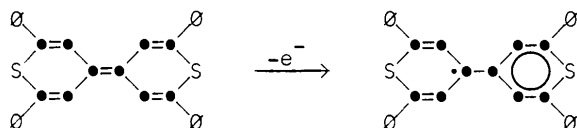

The Structure of Tetraphenyldithiapyranylidene*

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Abstract. $C_{34}H_{24}S_2$, $M_r = 496 \cdot 7$, monoclinic, $I2/a$, $a = 25 \cdot 090$ (4), $b = 5 \cdot 537$ (3), $c = 18 \cdot 067$ (4) Å, $\beta = 100 \cdot 17$ (2)°, $V = 2471$ (2) Å^3, $Z = 4$, $D_m = 1 \cdot 34$, $D_c = 1 \cdot 335$ Mg m^{-3}, λ(Mo $K\alpha$) = $0 \cdot 71073$ Å, μ(Mo $K\alpha$) = $0 \cdot 24$ mm^{-1}, $F(000) = 1040$. The structure was solved from diffractometer data by direct methods and refined by block-diagonal least squares to $R = 0 \cdot 055$. The centrosymmetric molecules are only approximately planar. The C(3)—C(3') bond joining the thiapyranylidene rings is 1·389 Å, and the chemically unique bonds in the rings average 1·745 for S—C(1), 1·339 for C(1)—C(2), and 1·441 Å for C(2)—C(3). These distances are consistent with a hybrid molecule composed of contributions of 50% from the uncharged species and 50% from charge-separated canonical structures involving an aromatic sextet.

Introduction. The title compound (φ_4DTP) can be oxidized to form a radical cation having an aromatic sextet (Perlstein, 1977):

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* Alternative name: 3,3′,5,5′-Tetraphenyl-4,4′-dithia-1,1′-bi-2,5-cyclohexadienylidene.

Such a material can function as a donor molecule in highly conducting organic charge-transfer salts. Ion-radical salts of φ_4DTP with TCNQ (Alizon *et al.*, 1977; Isett, Reynolds, Schneider & Perlstein, 1979a) and with iodide (Isett, Reynolds, Schneider & Perlstein, 1979b) have been prepared and the electrical properties investigated. We have recently completed studies of the crystal structures of two highly conducting iodide salts, φ_4DTP(I$_3$)$_{0.36}$(I$_5$)$_{0.40}$ (DTPI1) and φ_4DTP(I$_3$)$_{0.72}$ (DTPI2) (Luss & Smith, 1980), and report here the structure of φ_4DTP for comparison with the oxidized φ_4DTP ions.

Gold, prismatic crystals elongated along b were produced on cooling and evaporating a heated 6:1 THF:acetonitrile solution. Precession photographs showed systematic absences for hkl, $h + k + l$ odd, and $h0l$, h odd, which were consistent with space groups Ia and $I2/a$. The structure was successfully solved in $I2/a$.