Pyrylium Salts. VII. 2,4,6-Triphenyl-pyrylium Trichloroacetate

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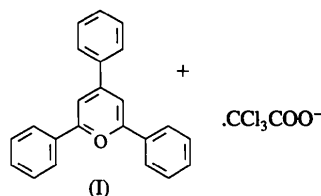*Department of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland*

Abstract

The structure of $C_{23}H_{17}O^+.C_2Cl_3O_2^-$ has been determined. The three benzene rings are planar, but tilt from the plane of the pyrylium ring at angles of 14.9, 23.7 and 6.1°, respectively. The C—C bond length in the anion is much longer than expected [1.579 (7) Å]. The aromatic character of the pyrylium ring is discussed.

Comment

As a continuation of our studies of substituent effects on the molecular geomery of 4'-substituted 2,4,6-triphenyl-pyrylium salts (Turowska-Tyrk, Krygowski, Milart, Butt & Topsom, 1991; Turowska-Tyrk, Krygowski & Milart, 1991; Krygowski, Anulewicz, Pniewska & Milart, 1991; Turowska-Tyrk, Anulewicz, Krygowski, Pniewska & Milart, 1992), we investigated crystals of the title compound to confirm the older data on the unsubstituted derivative (Tamamura, Yamane, Yasuoka & Kasai, 1974). The difference in anion does not significantly affect the molecular geometry of the cationic moiety. The aromatic character of the pyrylium ring, as estimated by its HOMA index (Krygowski, 1993), is 0.501, comparable with the value of 0.514 found for the unsubstituted species (Tamamura, Yamane, Yasuoka & Kasai, 1974) and higher than those of the NMe₂ (Turowska-Tyrk, Krygowski & Milart, 1991) and OH (Turowska-Tyrk, Anulewicz, Krygowski, Pniewska & Milart, 1992) derivatives, for which the HOMA values are 0.297 and 0.447, respectively. Evidently, electron-donating substituents increase the localization of double bonds in the pyrylium ring, reducing its aromatic character. The electron-accepting substituents NO₂ (Turowska-Tyrk, Krygowski, Milart, Butt & Topsom, 1991) and COOH (Krygowski, Anulewicz, Pniewska & Milart, 1991) increase the aromaticity of the pyrylium ring slightly; the HOMA values are 0.573 and 0.581, respectively.

The trichloroacetate anion has relatively short CO bonds [1.225 (6) and 1.233 (6) Å] and an anomalously long C—C bond [1.579 (7) Å]. This effect may be readily explained in terms of the Walsh–Bent rule (Bent, 1961). The more electronegative –CCl₃ group polarizes the sp^3 hybrid orbital along the C7—C8 bond into the $sp^{3+\delta}$ state. This is associated with a decrease of the $2p$ contribution in the sp^2 hybrid orbitals of the C—O bonds to the $sp^{2-\delta/2}$ state. As a result, lengthening of the C—C bond, shortening of the C—O bonds and an increase of the O—C—O bond angles should be observed. Such expected changes are confirmed by the observed bond lengths and angles.
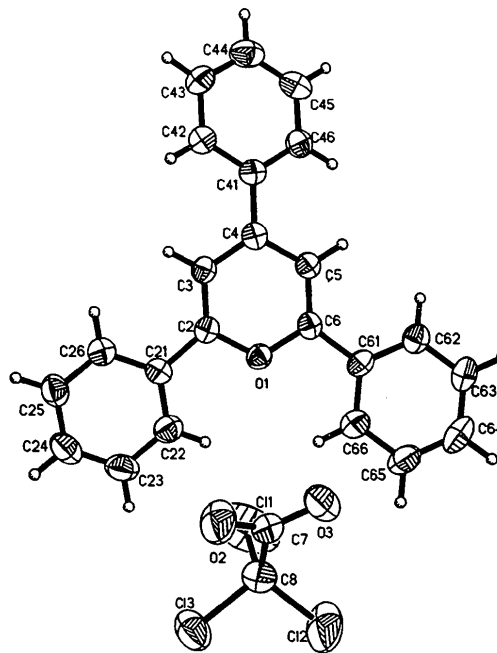

Fig. 1. View of the molecule showing the atomic numbering system. Ellipsoids are drawn at the 50% probability level.

Experimental

Crystal data

$C_{23}H_{17}O^+.C_2Cl_3O_2^-$	Cu $K\alpha$ radiation
$M_r = 471.77$	$\lambda = 1.54178$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 12.513 (2)$ Å	$\theta = 10-28°$
$b = 17.356 (3)$ Å	$\mu = 4.062$ mm^{-1}
$c = 10.172 (2)$ Å	$T = 293 (2)$ K
$\beta = 102.660 (3)°$	Prism

$V = 2155.4\,(7)$ Å^3
$Z = 4$
$D_x = 1.454$ Mg m^{-3}

$0.32 \times 0.32 \times 0.28$ mm
Yellow

Data collection

Kuma KM-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
  none
2563 measured reflections
2563 independent reflections
2454 observed reflections
  $[I > 2\sigma(I)]$

$\theta_{max} = 59.99°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 12$
3 standard reflections
  monitored every 100
  reflections
  intensity decay: $<5\%$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0681$
$wR(F^2) = 0.1770$
$S = 1.053$
2558 reflections
298 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0956P)^2 + 5.1989P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.568$ e Å^{-3}
$\Delta\rho_{min} = -0.835$ e Å^{-3}
Extinction correction:
  SHELXL93 (Sheldrick,
  1993)
Extinction coefficient:
  0.0007 (2)
Atomic scattering factors
  from International Tables
  for Crystallography (1992,
  Vol. C, Tables 4.2.6.8 and
  6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cl1	0.8280 (2)	0.52119 (14)	0.4160 (2)	0.1387 (11)
Cl3	0.78493 (12)	0.64852 (8)	0.2389 (2)	0.0700 (5)
Cl2	0.89305 (14)	0.52002 (11)	0.1583 (3)	0.1130 (9)
O2	0.5987 (3)	0.5494 (2)	0.1741 (5)	0.0725 (12)
O3	0.6849 (3)	0.4387 (2)	0.1530 (4)	0.0622 (10)
C7	0.6783 (4)	0.5070 (3)	0.1834 (5)	0.0440 (11)
C8	0.7918 (4)	0.5468 (3)	0.2445 (5)	0.0466 (12)
O1	0.7690 (2)	0.3686 (2)	0.7057 (3)	0.0340 (7)
C2	0.7026 (3)	0.4012 (2)	0.7785 (4)	0.0314 (9)
C3	0.6340 (3)	0.3566 (2)	0.8324 (4)	0.0352 (10)
C4	0.6304 (3)	0.2768 (2)	0.8118 (4)	0.0332 (10)
C5	0.6981 (3)	0.2456 (2)	0.7316 (4)	0.0342 (10)
C6	0.7678 (3)	0.2918 (2)	0.6815 (4)	0.0329 (9)
C21	0.7173 (3)	0.4847 (2)	0.7922 (4)	0.0341 (10)
C22	0.8086 (4)	0.5202 (3)	0.7619 (5)	0.0440 (11)
C23	0.8231 (5)	0.5989 (3)	0.7787 (5)	0.0558 (14)
C24	0.7475 (5)	0.6418 (3)	0.8252 (5)	0.0551 (14)
C25	0.6557 (4)	0.6071 (3)	0.8545 (5)	0.0499 (12)
C26	0.6410 (4)	0.5287 (3)	0.8394 (4)	0.0394 (11)
C41	0.5628 (3)	0.2266 (2)	0.8764 (4)	0.0334 (10)
C42	0.4717 (4)	0.2557 (3)	0.9178 (5)	0.0436 (11)
C43	0.4128 (4)	0.2084 (3)	0.9866 (5)	0.0539 (13)
C44	0.4442 (5)	0.1336 (3)	1.0151 (5)	0.0547 (13)
C45	0.5336 (4)	0.1041 (3)	0.9731 (5)	0.0498 (13)
C46	0.5914 (4)	0.1498 (2)	0.9022 (5)	0.0407 (11)
C61	0.8448 (3)	0.2688 (2)	0.6002 (4)	0.0351 (10)
C62	0.8616 (4)	0.1910 (3)	0.5766 (4)	0.0412 (11)
C63	0.9341 (4)	0.1697 (3)	0.4995 (5)	0.0503 (12)
C64	0.9914 (4)	0.2250 (4)	0.4455 (5)	0.0578 (14)
C65	0.9755 (5)	0.3013 (3)	0.4681 (6)	0.063 (2)
C66	0.9036 (4)	0.3235 (3)	0.5457 (5)	0.0558 (14)

Table 2. Selected geometric parameters (Å, °)

Cl1—C8	1.761 (5)	C22—C23	1.383 (7)
Cl3—C8	1.768 (5)	C23—C24	1.367 (8)
Cl2—C8	1.754 (5)	C24—C25	1.386 (7)
O2—C7	1.225 (6)	C25—C26	1.378 (6)
O3—C7	1.233 (6)	C41—C46	1.391 (6)
C7—C8	1.579 (7)	C41—C42	1.393 (6)
O1—C2	1.352 (5)	C42—C43	1.390 (7)
O1—C6	1.355 (5)	C43—C44	1.369 (7)
C2—C3	1.358 (6)	C44—C45	1.380 (7)
C2—C21	1.464 (6)	C45—C46	1.379 (7)
C3—C4	1.400 (6)	C61—C66	1.390 (7)
C4—C5	1.406 (6)	C61—C62	1.395 (6)
C4—C41	1.466 (6)	C62—C63	1.375 (7)
C5—C6	1.362 (6)	C63—C64	1.380 (8)
C6—C61	1.456 (6)	C64—C65	1.367 (8)
C21—C26	1.388 (6)	C65—C66	1.376 (7)
C21—C22	1.391 (6)		
O2—C7—O3	131.0 (5)	C22—C21—C2	120.6 (4)
O2—C7—C8	114.5 (4)	C23—C22—C21	120.1 (5)
O3—C7—C8	114.5 (4)	C24—C23—C22	119.9 (5)
C7—C8—Cl2	111.9 (3)	C23—C24—C25	120.5 (5)
C7—C8—Cl1	107.1 (3)	C26—C25—C24	120.1 (5)
Cl2—C8—Cl1	111.8 (3)	C25—C26—C21	119.8 (4)
C7—C8—Cl3	113.0 (3)	C46—C41—C42	119.0 (4)
Cl2—C8—Cl3	106.5 (3)	C46—C41—C4	120.2 (4)
Cl1—C8—Cl3	106.5 (3)	C42—C41—C4	120.8 (4)
C2—O1—C6	121.9 (3)	C43—C42—C41	119.8 (4)
O1—C2—C3	120.0 (4)	C44—C43—C42	120.5 (5)
O1—C2—C21	112.8 (3)	C43—C44—C45	120.0 (5)
C3—C2—C21	127.1 (4)	C46—C45—C44	120.2 (5)
C2—C3—C4	120.4 (4)	C45—C46—C41	120.5 (4)
C3—C4—C5	117.6 (4)	C66—C61—C62	118.7 (4)
C3—C4—C41	121.5 (4)	C66—C61—C6	120.9 (4)
C5—C4—C41	120.8 (4)	C62—C61—C6	120.4 (4)
C6—C5—C4	120.5 (4)	C63—C62—C61	120.1 (4)
O1—C6—C5	119.5 (4)	C62—C63—C64	120.4 (5)
O1—C6—C61	113.0 (3)	C65—C64—C63	119.9 (5)
C5—C6—C61	127.5 (4)	C64—C65—C66	120.4 (5)
C26—C21—C22	119.7 (4)	C65—C66—C61	120.5 (5)
C26—C21—C2	119.7 (4)		

Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$C_{23}H_{17}O^+.C_2Cl_3O_2^-$

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(I)

11,12-Seco-12,13-didehydromultiflorine Perchlorate Hydrate

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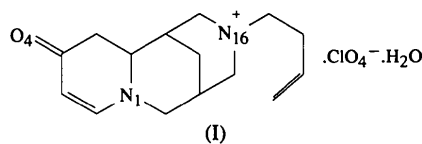
Abstract

The structure of 11,12-seco-12,13-didehydromultiflorine perchlorate hydrate [IUPAC name: 3-(but-3-enyl)-10-oxo-1,2,3,4,5,6,11,11a-octahydro-10*H*-1,5-methanopyrido[1,2-*a*][1,5]diazocinium perchlorate hydrate], $C_{15}H_{23}N_2O^+.ClO_4^-.H_2O$, a new alkaloid found in lupin plants, has been confirmed by X-ray analysis. The cation is formed by protonation of the butenyl-bonded N atom, N16. There is significant conjugation in the N1—C2=C3—C4=O4 fragment of the cation. The structure is partially disordered and the molecular packing is governed by a network of intermolecular hydrogen bonds.

Comment

An alkaloid extracted from the seeds of *Lupinus albus* (cultivar BAC) was found to have physical properties, including an IR spectrum, almost identical to those of the alkaloid known as *N*-methylalbine (Wiewiórowski & Wolińska-Mocydlarz, 1961, 1964). Investigation by means of ^{13}C NMR and mass spectroscopy suggested, however, that this compound has the same structure as 11,12-seco-12,13-didehydromultiflorine rather than that of *N*-methylalbine (Wysocka & Brukwicki, 1988). In order to corroborate this assignment, we have performed an X-ray structural analysis of the perchlorate salt of the alkaloid, (I). The results of these studies show the structure to be correct.

Ring *A* (Fig. 1) has a distorted half-chair conformation, with atoms C5 and C6 deviating significantly and in opposite directions from the least-squares plane through the remaining four atoms [the deviations are −0.181 (9) and 0.441 (8) Å for C5 and C6, respectively]. The planarity of the N1—C2=C3—C4=O4 system, as well as the pattern of bond lengths, indicates a noticeable conjugation within the system. The *A*/*B* ring junction has a *trans* configuration [torsion angles C2—N1—C6—C5 −41.5 (5) and C7—C6—N1—C10 46.8 (5)°]. Ring *B* adopts a distorted chair conformation. A similar configurational/conformational pattern for the *A*/*B* ring system was observed in the structures of both multiflorine (Kubicki & Borowiak, 1989) and the multiflorine cation (Pyżalska, Gdaniec, Borowiak & Wolińska-Mocydlarz, 1980). Ring *C* of the title compound has a distorted chair conformation, as in the multiflorine cation, while in the multiflorine free base it has a boat conformation. This conformational change, also observed in sparteine derivatives (Kubicki, Borowiak & Boczoń, 1991, and references therein), accompanied by the inversion of configuration about the N16 atom, is a result of protonation at atom N16 and subsequent formation of the intramolecular (sparteine) or intermolecular (multiflorine) hydrogen bonds. Therefore, it would be possible for the same type of inversion to take place in
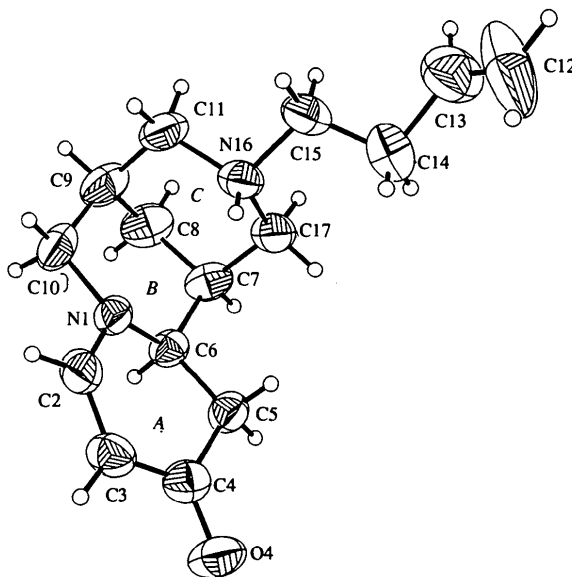

Fig. 1. Displacement ellipsoid representation of the title cation with the labelling scheme. The ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.