C11—C12—C13—C14	68.7 (2)	C12—C13—C14—C15	−57.6 (2)
C11—C16—C15—C14	48.6 (3)	C13—C12—C11—C16	−18.6 (2)
C12—C11—C16—C15	−38.4 (3)	C13—C14—C15—C16	0.9 (2)

All H-atom positions were calculated geometrically, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom). Refinements were based on all the independent reflections. The threshold $I > 2\sigma(I)$ was used only for calculation of the *R* factor. In (I), there is an orientational disorder of a methylacrylate moiety in one of the two independent molecules; this disorder is similar to that observed in (*E*)-stilbenes and other related compounds (Harada *et al.*, 1997). The central C=C double bond has two possible orientations which are approximately perpendicular to each other, and the terminal COOMe moiety is only a little rotated in its plane. The site-occupancy factors of these two possible sets of positions, C19=C20—C21(=O4)—O5—C22 and C119=C120—C121(=O104)—O105—C122, were assumed to be 80 and 20%, respectively, and the atoms in the minor part were refined isotropically. H atoms were not introduced for the minor part.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1998); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1086). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Becker, H.-D., Skelton, B. W. & White, A. H. (1981). *J. Chem. Soc. Perkin Trans.* pp. 442–446.

Cambridge Structural Database (1998). Version 5.16. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Harada, J., Ogawa, K. & Tomoda, S. (1997). *Acta Cryst.* B**53**, 662–672.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Jones, D. S. & Karle, I. L. (1974). *Acta Cryst.* B**30**, 617–623.

Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1998). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.9. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Nishiyama, A., Eto, H., Terada, Y., Iguchi, M. & Yamamura, S. (1983). *Chem. Pharm. Bull.* **31**, 2820–2833.

Sasaki, K. & Hirata, Y. (1974). *Acta Cryst.* B**30**, 1619–1620.

Sasaki, K., Hirata, Y., Yamamura, S., Chen, Y., Hong, M. & Hsu, H. (1973). *Tetrahedron Lett.* **49**, 4881–4884.

Yamamura, S., Terada, Y., Chen, Y.-P., Hong, M., Hsu, H.-Y., Sasaki, K. & Hirata, Y. (1976). *Bull. Chem. Soc. Jpn*, **49**, 1940–1948.

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Diisopropylammonium diphenylmethylnitronate at 200 K

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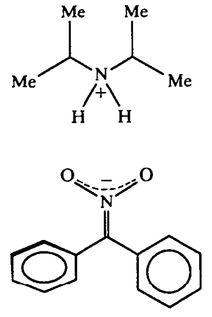
Abstract

In the crystal structure of the title compound, $C_6H_{16}N^+\cdot C_{13}H_{10}NO_2^-$, the ions are arranged in quadruples, in which two cations and two anions form a cyclic hydrogen-bonded system.

Comment

The structure of diisopropylammonium diphenylmethylnitronate, (I), is of particular interest owing to the formation of a 12-membered macrocycle containing four polar hydrogen-bond bridges N—H···O, which due to their cooperative effect provide an example of molecular self-organization. Crystals are obtained as colourless prisms from the reaction mixture of *aci*-nitrodiphenylmethane (Colvin *et al.*, 1980; Konowalow, 1896) with diisopropylamine at 258 K. Sets of two symmetry-equivalent protonated molecular cations and two equivalent anions form hydrogen-bonded molecular-ion quadruples within undulating layers parallel to the *xy* plane (Fig. 1). The packing is supported by additional weak C—H···π



(I)

interactions. The symmetry-equivalent ion-pairs of a quadruple are connected by N—H···O hydrogen bonds to produce 12-membered rings (···ONO···HNH···)$_2$. The CNO_2 planes of the anions are shifted perpendicular to each other by 2.09 (1) Å and exhibit an interplanar angle of 29 (2)° relative to the planar rectangle of the four O atoms. The amine-N atom centres deviate ±0.74 (1) Å from this plane, resulting in the twisting of the 12-membered ring. The protonated nitrogen centre N2 forms a hydrogen bond N2—H2*A*···O1 with a distance N···O of 2.725 (3) Å and an angle of 169 (2)°. The second crystallographically independent hydrogen bond N2—H2*B*···O2($-x$, $1-y$, $1-z$) shows a distance of 2.710 (3) Å and an angle of 170 (2)°. The diisopropylammonium cation exhibits a staggered conformation with the central angle C2—N2—C5 expanded by 8° compared to an ideal tetrahedron. The phenyl substituents of the nitronate anions are orientated differently with one of them approximately coplanar to the plane CNO_2 and the other in a nearly perpendicular orientation with a torsion angle of 88.6 (2)° around the C1—C21 bond. Due to steric hindrance, the angle N1—C1—C11 is widened to 124.5 (2)°, reducing the corresponding angle N1—C1—C21 to 115.2 (2)°. The distance between the planar coordinated centres, C1 and N1, amounts to 1.322 (2) Å and the N—O bonds with distances of 1.302 (2) and 1.308 (2) Å are almost identical. This conformation of the nitronate group is in agreement with that in other nitronate anions such as hexa(*aci*-9-nitrofluorenepotassium)bis(tetrahydrofuran)dioxane (Bock *et al.*, 1995). The torsion angles of the phenyl rings differ considerably from those found in the structure of neutral *aci*-nitrodiphenylmethane (Bock *et al.*, 1993).

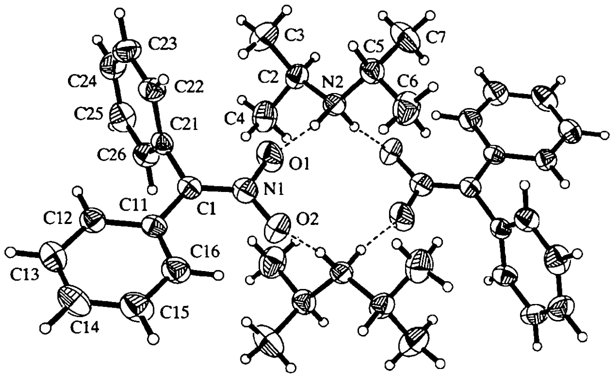


Fig. 1. Two cations and two anions arranged around an inversion centre, showing the hydrogen bonding, the atom labels of the asymmetric unit and 50% probability ellipsoids.

Experimental

A cooled suspension of sodium diphenylmethylnitronate (0.5 g, 2.1 mmol) in water (20 ml) was acidified with 5% sulfuric acid to pH 2. The immediately precipitating pale pink *aci*-nitrodiphenylmethane was filtered, washed three times with cold water, dissolved in diethyl ether (40 ml) and the solution dried with sodium sulfate. After removal of the sodium sulfate by filtration, diisopropylamine (0.3 ml, 2.1 mmol) was added to the solution at 273 K. The resulting clear yellow solution was cooled to 258 K. Crystals suitable for an X-ray crystal structure determination grew after one day. They were washed three times with small amounts of *n*-hexane and dried *in vacuo*. Analysis, found: C 72.37, H 8.71, N 8.71%; calculated: C 72.58, H 8.33, N 8.91%; m.p. 348–349 K (Kofler, uncorrected).

Crystal data

$C_6H_{16}N^+ \cdot C_{13}H_{10}NO_2^-$
$M_r = 314.42$
Triclinic
$P\overline{1}$
$a = 9.198\ (1)$ Å
$b = 10.559\ (1)$ Å
$c = 10.593\ (1)$ Å
$\alpha = 68.94\ (1)°$
$\beta = 79.01\ (1)°$
$\gamma = 67.41\ (1)°$
$V = 884.8\ (2)$ Å^3
$Z = 2$
$D_x = 1.180$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 7.5$–$17.5°$
$\mu = 0.077$ mm^{-1}
$T = 200\ (2)$ K
Prism
0.46 × 0.36 × 0.18 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω/θ scan
Absorption correction: none
3538 measured reflections
3307 independent reflections
2305 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$

$\theta_{\max} = 26.5°$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.114$
$S = 1.022$
3306 reflections
226 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 0.2790P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.163$ e Å^{-3}
$\Delta\rho_{\min} = -0.150$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.018 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—O1	1.302 (2)	C1—C21	1.493 (2)
N1—O2	1.308 (2)	N2—C2	1.499 (2)
N1—C1	1.322 (2)	N2—C5	1.502 (2)
C1—C11	1.468 (2)		
O1—N1—O2	116.60 (15)	N1—C1—C21	115.24 (15)
O1—N1—C1	120.0 (2)	C11—C1—C21	120.3 (2)
O2—N1—C1	123.39 (15)	C2—N2—C5	117.32 (15)
N1—C1—C11	124.5 (2)		
O2—N1—C1—C11	0.4 (3)	N1—C1—C11—C16	4.7 (3)
O1—N1—C1—C21	−0.3 (2)	C11—C1—C21—C22	88.1 (2)

The H(—N) atoms were refined freely, while a riding model was used for all other H atoms, with $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$.

Data collection: *XSCANS* (Siemens, 1994*a*). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*94 (Sheldrick, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1289). Services for accessing these data are described at the back of the journal.

References

Bock, H., Dienelt, R., Schoedel, H. & Havlas, Z. (1995). *Tetrahedron Lett.* **43**, 7855–7858.

Bock, H., Dienelt, R., Schoedel, H., Havlas, Z., Herdtweck, E. & Herrmann, W. A. (1993). *Angew. Chem.* **105**, 1826–1828; *Angew. Chem. Int. Ed. Engl.* **32**, 1758–1760.

Colvin, E. W., Beck, A. K., Bastani, B., Seebach, D., Yasushi, K. & Dunitz, J. D. (1980). *Helv. Chim. Acta*, **63**, 697–710.

Konowalow, M. (1896). *Ber. Dtsch Chem. Ges.* **29**, 2193–2198.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1994). *SHELXS94. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Siemens (1994*a*). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994*b*). *XP. Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Pyridinium and 1,2-diazinium salts of chloranilic acid

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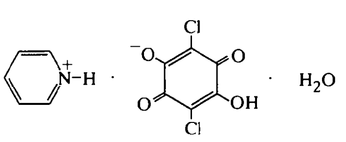
Abstract

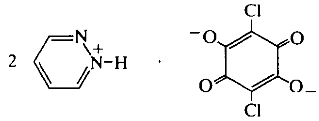
The crystal structures of two salts of chloranilic acid (2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone), namely pyridinium chloranilate monohydrate, $C_5H_6N^+\cdot C_6HCl_2O_4^-\cdot H_2O$, (I), and bis(1,2-diazinium) chloranilate, $2C_4H_5N_2^+\cdot C_6Cl_2O_4^{2-}$, (II), have been determined at room temperature. In (I) and (II), the cations and anions are held together by N—H···O hydrogen bonds with short N···O distances of 2.670 (4) Å in (I) and 2.582 (3) Å in (II). The H atom in the hydrogen bond in (I) was located at the N-atom site [N—H = 1.09 (5) and H···O = 1.70 (5) Å], while that in (II) was found near the center of N···O [N···H = 1.32 (5) and H···O = 1.28 (5) Å].

Comment

Several hydrogen-bonded complexes of the chloranilic acid–amine (1:1) system have been studied by IR (Issa *et al.*, 1991) and by IR, NMR and UV (Habeeb *et al.*, 1995). Habeeb *et al.* reported that the hydrogen bonds formed between chloranilic acid and amines vary from an N—H···O to an N···H—O type with decreasing pK_a values of the amines. The title compounds, (I) and (II), were investigated as part of a structural study on hydrogen bonding in chloranilic acid–amine systems. The pK_a values of pyridine and 1,2-diazine (pyridazine) are 5.2 and 2.3, respectively.



(I)



(II)

An asymmetric unit of (I) is composed of $C_5H_6N^+\cdot C_6HCl_2O_4^-\cdot H_2O$ and that of (II) is $C_4H_5N_2^+\cdot\frac{1}{2}C_6Cl_2O_4^{2-}$. The chloranilate ions in (I) and (II) show characteristic structures having four short C—C bonds

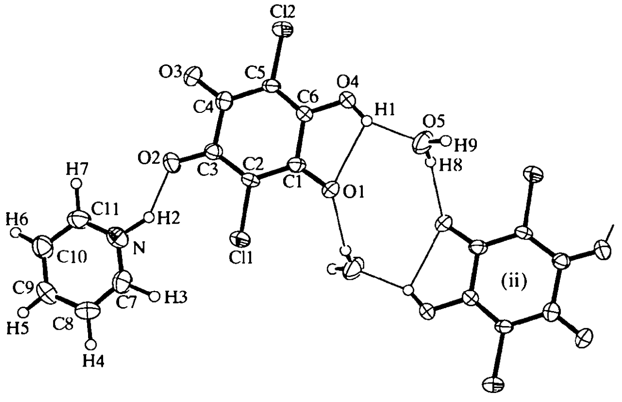


Fig. 1. *ORTEP*II (Johnson, 1976) view of (I), showing the atomic numbering. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are drawn as spheres with $B_{\mathrm{iso}} = 1.0$ Å^2. Hydrogen bonds are indicated by thin lines [symmetry code: (ii) $1-x$, $1-y$, $1-z$].