Quinolinium dichromate, $[C_9H_7NH^+]_2 \cdot Cr_2O_7{}^{2-}$

T. V. Sundar,[a] V. Parthasarathi,[b]*
S. Thamotharan[b] and
K. G. Sekar[c]

[a]Department of Physics, National College, Tiruchirappalli 620 001, India, [b]Department of Physics, Bharathidasan University, Tiruchirappalli 620 024, India, and [c]Department of Chemistry, National College, Tiruchirappalli 620 001, India.

Correspondence e-mail: vpsarati@yahoo.com

Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.008 Å
R factor = 0.056
wR factor = 0.162
Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $(C_9H_8N)_2[Cr_2O_7]$, crystallizes in the monoclinic space group $P2_1/c$, with eight cations and four anions in the unit cell. The quinolinium cations and a dichromate anion are connected through N—H···O and C—H···O intermolecular hydrogen bonds and by aromatic π–π-stacking interactions. The dichromate geometry is normal, with a Cr—O(bridging)—Cr angle of 135.1 (2)°.

Comment

The X-ray study of quinolinium dichromate (QDC), (I), was undertaken in order to study the hydrogen-bond patterns and crystal packing. QDC is reported to be a selective oxidant for a wide range of substrates in view of its ease of preparation and high stability (Balasubramanian & Prathiba, 1986; Karim & Mahanti, 1992; Aruna *et al.*, 1994; Aruna & Manikyamba, 1995; Ravishankar *et al.*, 1998; Kharnaior *et al.*, 2001; Lyngdoh *et al.*, 2001).

(I)
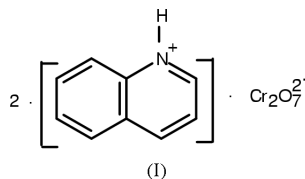
In QDC, two heterocyclic quinolinium cations and a dichromate anion are connected through N—H···O and C—H···O intermolecular hydrogen bonds. The asymmetric unit and the numbering scheme are shown in Fig. 1. The quinolinium cations form π–π-stacking interactions. One of the six-membered rings, with centroid $Cg1$ (defined by atoms N1, C11–C13, C18 and C19), of the quinolinium cation at (x, y, z) has a π–π interaction with one of the six-membered rings, with centroid $Cg4$ (defined by atoms C24–C29), at $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ of another quinolinium cation. The other six-membered ring, with centroid $Cg3$ (defined by atoms C14–C19), has a π–π contact with centroid $Cg2$ (defined by atoms N2, C21–C23, C28 and C29) of the quinolinium cation which belongs to the same asymmetric unit. The distances between the ring centroids are listed in Table 1. The quinolinium rings are stacked along the the c axis, having their planes nearly parallel to the (001) plane (Fig. 2), as is evident from the fact that the dihedral angle between their least-squares planes is 2.87 (9)°. The corresponding bond lengths of the two quinolinium rings are in very good agreement. The largest difference in bond length is observed in the bonds C16—C17 [1.333 (8) Å] and C26—C27 [1.356 (7) Å]. The agreement is also good for the corresponding angles in the rings, with maximum difference between C11—N1—C18 [122.2 (5)°] and C21—N2—C28 [123.3 (4)°]. However, these differences are
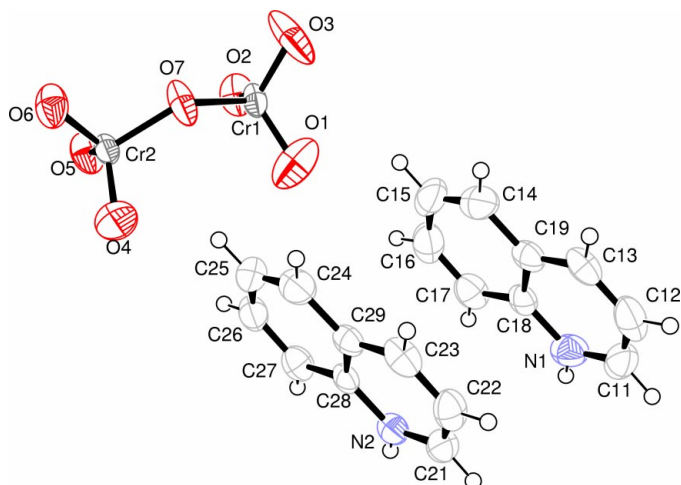
Figure 1
The asymmetric unit of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
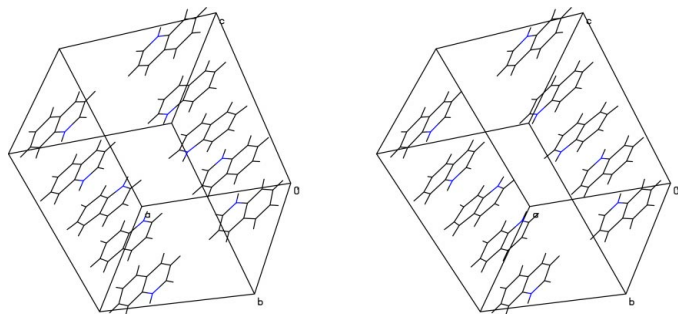

Figure 2
Stereoview of part of the crystal structure of (I), showing the stacking of quinolinium rings along the c axis. Dichromate anions are omitted for clarity.

not significant, as they are well within the 3σ level. Also, the bond distances and angles of the molecule are reasonably comparable with values in compounds containing a similar quinazoline ring and are in agreement with related structures (Dobson & Gerkin, 1999a,b; Rajnikant et al., 2002).

The dichromate anion consits of two CrO_4 tetrahedra sharing one O atom (the bridge atom O7). The CrO_4 groups are slightly distorted tetrahedra. The distances of the chromium atoms from the bridging oxygen, O7, are 1.793 (3) (Cr1—O7) and 1.804 (3) Å (Cr2—O7). The other Cr—O distances range from 1.572 (5) (Cr1—O1) to 1.615 (3) Å (Cr2—O6). The dichromate geometry is normal for Cr1—O7—Cr2 [135.1 (2)°]. The angles O3—Cr1—O7 [103.9 (2)°] and O6—Cr2—O7 [103.92 (17)°] differ significantly from tetrahedral geometry, 109.5°. A similar deviation is described for analogous sulfates in the paper by Brown (1973), where two types of angular distortions occur, known as the bond-length effect and the configurational effect. In the present case, the bond-length effect is not observed, since the O atoms are not in contact, but the configurational effect is observed. There is no significant deviation in the bond angles and distances of the dichromate anion from the values in
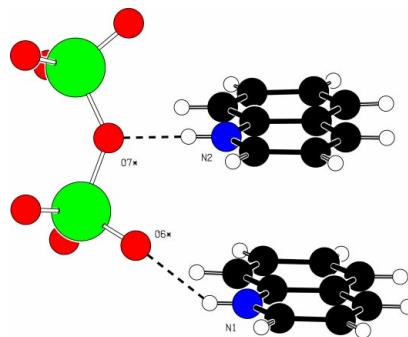

Figure 3
Part of the crystal structure of (I), showing N—H···O interactions.

similar structures reported in the literature (Panagiotopoulos & Brown, 1972; Dahan, 1975; Blum et al., 1980).

Details of the N—H···O (Fig. 3) and C—H···O (Fig. 4) interactions are presented in Table 2. As seen from Table 2, for (I), atoms N1 and N2 act as hydrogen-bond donors and form N—H···O intermolecular interactions with atoms O6 and O7 of an adjacent anion. H11 on C11 is involved in a weak intermolecular C—H···O interaction with the terminal atom O6 of the adjacent dichromate anion and H13 on C13 is involved in a weak intermolecular C—H···O interaction with another terminal atom, O3, of another anion. These interactions produce a continuous chain, which runs parallel to the c axis. Atom C21 forms a weak C—H···O intermolecular interaction with O2 of a neighbouring centrosymmetrically-related anion. Apart from intermolecular hydrogen bonds, the structure is also stabilized by π–π-stacking interactions (Table 1).

Experimental

QDC was prepared as reported in the literature (Balasubramanian & Prathiba, 1986). To a stirred solution of CrO_3 (10 g) in water (10 ml), cooled in ice, was added quinoline (9 ml), in small portions. The solution was diluted with acetone (40 ml), cooled to 253 K and the orange solid which separated out was filtered off, washed with acetone, dried in vacuo and recrystallized from water (m.p. 433 K, yield 72%).

Crystal data

$(C_9H_8N)_2[Cr_2O_7]$	$D_x = 1.695$ Mg m^{-3}
$M_r = 476.33$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 12.286$ (5) Å	reflections
$b = 9.965$ (3) Å	$\theta = 2.0$–$25.0°$
$c = 15.386$ (5) Å	$\mu = 1.21$ mm^{-1}
$\beta = 97.67$ (3)°	$T = 293$ (2) K
$V = 1866.9$ (11) Å^3	Needle, orange–red
$Z = 4$	$0.30 \times 0.20 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.034$
diffractometer	$\theta_{max} = 25.0°$
Non-profiled $\omega/2\theta$ scans	$h = 0 \rightarrow 14$
Absorption correction: ψ scan	$k = 0 \rightarrow 11$
(North et al., 1968)	$l = -18 \rightarrow 18$
$T_{min} = 0.713$, $T_{max} = 0.889$	2 standard reflections
3447 measured reflections	frequency: 60 min
3283 independent reflections	intensity decay: none
2210 reflections with $I > 2\sigma(I)$	
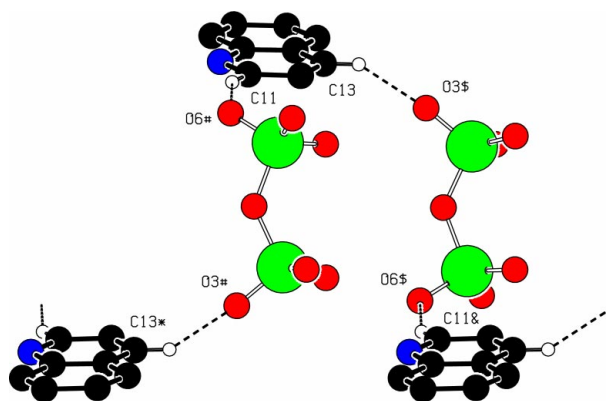
Figure 4
Part of the crystal structure of (I), showing the formation of a chain through C—H···O interactions. Atoms marked with a hash (#), an asterisk (*), a dollar sign ($) or an ampersand (&) are at the symmetry positions $(1 - x, 1 - y, -z)$, $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, $(x, \frac{1}{2} - y, -\frac{3}{2} + z)$ and $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

All H atoms were placed in geometrically idealized positions, N—H = 0.86 Å and C—H = 0.93 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(N)$ and $1.2U_{eq}(C)$. The maximum electron-density peak lies 1.03 Å from Cr2.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *WinGX* (Version 1.64.02; Farrugia, 1999) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0975P)^2 + 1.1704P]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.162$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rho_{max} = 1.12$ e Å^{-3}
3283 reflections	$\Delta\rho_{min} = -0.57$ e Å^{-3}
262 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

$Cg1-Cg4$	3.667 (3)	$Cg2-Cg3$	3.609 (3)
O1—Cr1—O7—Cr2	−71.5 (4)	O6—Cr2—O7—Cr1	−160.3 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O6^i	0.86	2.14	2.871 (5)	143
N2—H2···O7^i	0.86	1.82	2.676 (5)	179
C11—H11···O6^{ii}	0.93	2.39	3.254 (7)	154
C13—H13···O3^{iii}	0.93	2.17	2.976 (6)	144
C21—H21···O2^{iv}	0.93	2.43	3.189 (6)	139
C24—H24···O1	0.93	2.55	3.413 (8)	154

Symmetry codes: (i) $x, y - 1, z$; (ii) $1 - x, 1 - y, -z$; (iii) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (iv) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

References

Aruna, K. & Manikyamba, P. (1995). *Indian J. Chem. Sect. A*, **34**, 822–825.
Aruna, K., Manikyamba, P. & Sundaram, E. V. (1994). *Indian J. Chem. Sect. A*, **33**, 854–856.
Balasubramanian, K. & Prathiba, V. (1986). *Indian J. Chem. Sect. B*, **25**, 326–327.
Blum, P. D., Durif, A. & Guitel, J. C. (1980). *Acta Cryst.* B**36**, 137–139.
Brown, I. D. (1973). *Acta Cryst.* B**29**, 1979–1983.
Dahan, F. (1975). *Acta Cryst.* B**31**, 423–426.
Dobson, A. J. & Gerkin, R. E. (1999a). *Acta Cryst.* C**55**, 935–937.
Dobson, A. J. & Gerkin, R. E. (1999b). *Acta Cryst.* C**55**, 1192–1195.
Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.
Karim, E. & Mahanti, M. K. (1992). *Pol. J. Chem.* **66**, 1471–1476.
Kharnaior, G. G., Chaubey, G. S. & Mahanti, M. K. (2001). *Oxid. Commun.* **24**, 377–381.
Lyngdoh, C. B., Das, S. & Mahanti, M. K. (2001). *Oxid. Commun.* **24**, 382–387.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Panagiotopoulos, N. Ch. & Brown, I. D. (1972). *Acta Cryst.* B**28**, 2880–2882.
Rajnikant, V., Gupta, V. K., Suri, O. P. & Lal, M. (2002). *Ind. J. Pure Appl. Phys.* **40**, 59–61.
Ravishankar, M., Sekar, K. G. & Palaniappan, A. N. (1998). *Afinidad*, **477**, 357–362.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2002). *PLATON*. Version of April 2002. Utrecht University, The Netherlands.